Quantum Mechanics: Notes

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These notes on Quantum Mechanics currently follow no particular order. Please do feel free to provide feedback, error reports, etc.

1 History

The following points (very briefly!) summarize the development of quantum theory. Mainly from Weinberg's Chapter 1 [2].

Particle character of photons

- *Black body radiation* Energy density ρ of photon bath at temperature T per angular frequency ω measured in the late 1800's. Planck showed that the experimental results may be fit to the formula

$$\rho \equiv \frac{\mathrm{d}E}{\mathrm{d}V\mathrm{d}\omega} = \frac{\hbar}{\pi^2}\frac{\omega^3}{\exp(\hbar\omega/(k_{\mathrm{B}}T))-1}. \tag{1.0.1}$$

  This is where Planck's constant h (note: $\hbar \equiv h/(2\pi) \approx 1.054\cdots\times 10^{-34}$J s $= 6.582\cdots\times 10^{-22}$MeV s) was first discovered. Nowadays the presence or absence of $\hbar$ or h in physical predictions is oftentimes used as a zeroth-order indication of whether the effect under consideration is quantum or classical.

  Theoretical explanations tend to predict: *ρ blows up* at high frequency if we assume photons are classical waves. Planck's derivation assumed photons were coupled to a large number of discrete harmonic oscillators at temperature T. The (correct) derivation was made by Lorentz, by combining Gibbs' statistical mechanical arguments with Einstein's postulate that light was made of particles (see below) each with energy $\hbar\omega$. Namely, the hypothesis that photons are particles instead of waves changed the energy spectrum drastically at high frequencies.

- *Photoelectric effect* Einstein postulated photons – though it was G.N.Lewis who coined the name 'photon' itself – to explain photoelectric effect. Individual photons need to have energy larger than electron 'work function'. Otherwise no electrons emitted from metal. Millikan did experiment to verify emitted electron energy is $h\Delta\nu$, and obtained a h close to that occuring in Planck's black body formula.

- *Compton scattering* If photons were particles, they would collide/scatter electrons according to simple laws of kinematics obeying conservation of energy and momentum. Such scatterings between X-ray photons and electrons were done by Compton – and thus further solidified the particle nature of photons.

- *Remark on photons and probabilistic QM* The particle character of photons, together with the phenomenon of how the intensity of polarized light passing through a polarizer varies with the angle/orientation of the latter, can be used to argue for the probabilistic character of quantum mechanics – see lecture here for elaboration.

Atomic Physics & Wave Functions

- *Discrete character of Atomic Spectra* In the 1800's and early 1900's, the discrete character of the emission/absorption spectral lines from hot gases was not understood. These lines formed a pattern that can be used to identify different chemical compositions. For instance, Helium was in fact first discovered through the observation of its spectral lines on the chromosphere of the Sun.

- *Atomic Structure* Understanding atomic spectra required understanding atomic structure. Rutherford, Geiger, Marsden did experiments to suggest, the atom is comprised of a very heavy but small positively-charged nucleus, with much lighter but negatively-charged electrons orbiting it. Later on Moseley found experimental evidence that the nucleus is an integer multiple Z of $|e|$, the magnitude of the charge of the electron. (Rutherford coined the term 'proton'.) But Z was not A, the atomic weight; it was Chadwick who then discovered the electrically neutral neutrons. Hence: nucleons were Z protons and $A - Z$ neutrons.

  Classical electrodynamics would have predicted such a system to be radiatively unstable. Nonetheless Bohr, and later one Sommerfeld, invented quantization rules that allowed one to compute the discrete atomic energy levels. Of course, these rules are now superceded by quantum mechanics proper.

- *de Broglie, Schrödinger & Heisenberg* Since light, which previously was thought to be waves, are found to be particles as well – de Broglie suggested that electron (which were known to be particles) are perhaps waves as well. This idea can heuristically be connected to the Bohr-Sommerfeld quantization rules. Davisson and Germer carried out an experiment in 1927 to show the reality of electron waves, obtaining diffraction peaks from scattering electrons off a crystal of nickel (similar to X ray diffraction patterns).

  de Broglie's waves were for free particles. It was Schrödinger who then extended the ideas to allow the wave to interact with a potential (the Coulomb potential for atomic electrons). Thus quantum mechanic is born.

  Around the same time, Heisenberg devised his matrix mechanics, which came to be recognized as a complementary approach to quantum mechanics to the Schrödinger equation.

- *Dirac & QFT* The linear algebraic formulation we shall adopt, which subsumes both Schrödinger and Heisenberg, is due to Paul Dirac [1]. Dirac is also the pioneer of quantum field theory, the application of the rules of quantum mechanics to *fields*.

Probabilistic character of QM

- *Max Born* Even though quantum mechanics was devised by people like Schrödinger and Heisenberg, it was Born was recognized the Schrödinger wave function squared described the *probability* (per unit volume) the particle could be found at a given location. This is the radical departure from classical physics that bothered many – including Einstein.

Warning: For the rest of these notes, I am setting $\hbar = c = k_{\rm B} = 1$.

2 Basic Principles of Quantum Mechanics

Quantum Mechanics is the basic framework underlying the fundamental laws of Nature. Its basic principles are intimately tied to Linear Algebra.

Hilbert Space Given a physical system, its possible states are vectors in an abstract vector space, usually dubbed 'Hilbert space'. This can be finite or infinite dimensional. Moreover, all information of the physical system are fully contained within the ket it corresponds to.

Observables as Hermitian Operators Many physical observables in quantum mechanics – such as energy, position, momentum, spin, etc. – are described by Hermitian linear operators. The possible outcomes of measuring these observables are the eigenvalues of these Hermitian operators.

To properly describe a quantum system usually means to find as many mutually commuting observables as possible.

Born Rule Consider an observable A, with eigenstate $|\lambda\rangle$. When an experimentalist tries to measure A, the probability that the system described by $|\psi\rangle$ will be found in state $|\lambda\rangle$ – and thereby yield λ as the observable – is given by

$$P\left(|\psi\rangle \to |\lambda\rangle\right) = |\langle\lambda|\,\psi\rangle|^2 \tag{2.0.1}$$

provided both $|\psi\rangle$ and $|\lambda\rangle$ have been normalized to unit length.

If λ refers to a continuous set of eigenvalues, then $|\langle\lambda|\,\psi\rangle|^2$ would instead be a probability density – for example, $|\langle\vec{x}|\,\psi\rangle|^2$ is the probability per unit spatial volume for finding the quantum system at $\vec{x}$, because $|\vec{x}\rangle$ is the position eigenstate infinitely sharply localized at $\vec{x}$.

Because of this probabilistic interpretation of quantum mechanics, quantum states $\{|\psi\rangle\}$ are really rays in a Hilbert space. If $|\psi\rangle$ describes the system at hand, the probability of finding it in the state $|\psi\rangle$ is unity by assumption. This only fixes its length-squared $|\langle\psi|\,\psi\rangle|^2 = 1$; there is no other way to distinguish between $e^{i\delta}\,|\psi\rangle$ and $|\psi\rangle$, for real δ, and we are thus obliged to identify all vectors differing only by an overall phase as corresponding to the same system.

Copenhagen The Copenhagen interpretation of quantum mechanics further states that, upon such a measurement, the original state $|\psi\rangle$ 'collapses' to $|\lambda\rangle$ if indeed the observable turned out to be λ – at least for non-degenerate $|\lambda\rangle$. Suppose the system were degenerate, so that the eigen-subspace corresponding to the eigenvalue λ can be further labeled by say σ, we may denote these states as $\{|\lambda;\sigma\rangle\}$. Now, if $|\psi\rangle$ is some superposition of these λ-states, namely

$$|\lambda'\rangle \equiv \sum_\sigma C_\sigma\,|\lambda;\sigma\rangle \qquad\qquad (C_\sigma \in \mathbb{C}) \tag{2.0.2}$$

plus other states with eigenvalues not equal to λ; then upon measuring A, if the experimentalist finds λ, the state collapses instead to this $|\lambda'\rangle$:

$$|\psi\rangle \to \frac{|\lambda'\rangle}{\sqrt{\langle\lambda'|\,\lambda'\rangle}}. \tag{2.0.3}$$

Dynamics There is a 'total energy' operator, the Hamiltonian H, such that the time evolution of a state $|\psi(t)\rangle$ describing some physical system is governed by the Schrödinger equation:

$$i\partial_t\,|\psi(t)\rangle = H\,|\psi(t)\rangle\,, \tag{2.0.4}$$

in units where $\hbar = 1$.[1] Physically speaking, quantum mechanics is really a framework; the actual physical content of a given quantum theory is encoded within its Hamiltonian. This is analogous to Newton's laws of mechanics; in particular, "force equals mass times acceleration" is the classical parallel to eq. (2.0.4) – the physics of Newton's 2nd law is really specified by the actual form of the force law.

3 Time Evolution in Quantum Mechanics

Unitary Nature of Quantum Time Evolution In quantum mechanics, the physical system is described by a state $|\psi\rangle$ in some Hilbert space. Suppose we identify some observable A. We know its eigenstates $\{|\lambda\rangle\}$ span the whole space, and therefore we may exploit the completeness relation $\mathbb{I} = \sum_\lambda |\lambda\rangle \langle\lambda|$ to express

$$|\psi\rangle = \sum_\lambda |\lambda\rangle \langle\lambda|\psi\rangle . \tag{3.0.1}$$

The probability for finding the system a given state $|\lambda'\rangle$ is $|\langle\lambda'|\psi\rangle|^2$. On the other hand, the probability to find it in *any* arbitrary state must be one, since these eigenstates span the whole space.

$$1 = \sum_\lambda |\langle\lambda|\psi\rangle|^2 = \sum_\lambda \langle\psi|\lambda\rangle \langle\lambda|\psi\rangle = \langle\psi|\psi\rangle \tag{3.0.2}$$

In other words, the state itself must have unit norm. Not only that, it must do so for all time. Otherwise, it would mean the probably of find it in *any* state is less than 1. (Where would it be, then?) As we see now the time evolution is unitary – probability is conserved – iff the Hamiltonian is Hermitian.

The time-evolution equation carries Schrödinger's name:

$$i\partial_t |\psi\rangle = H|\psi\rangle , \tag{3.0.3}$$

$$-i\partial_t \langle\psi| = \langle\psi| H^\dagger . \tag{3.0.4}$$

Consider now

$$\partial_t (\langle\psi|\psi\rangle) = (\partial_t \langle\psi|)|\psi\rangle + \langle\psi|(\partial_t|\psi\rangle) = i\langle\psi|H^\dagger|\psi\rangle - i\langle\psi|H|\psi\rangle \tag{3.0.5}$$

$$= i\langle\psi|H^\dagger - H|\psi\rangle . \tag{3.0.6}$$

[2]If we want $\langle\psi|\psi\rangle = 1$ to remain one for all time; its time derivative must be zero. Since this must be true for any quantum state $|\psi\rangle$, we conclude

$$H = H^\dagger . \tag{3.0.7}$$

[1]Eq. (2.0.4) is the starting point for quantum dynamics. Often though – particularly in quantum field theory – one then quickly switches to the 'Heisenberg picture', where by choosing the analog of a rotating basis, the time evolution is then transferred onto the operators.
Also notice how i occurs explicitly in Schrödinger's equation; complex numbers are a necessity in quantum dynamics.

[2]You might wonder why $-i\partial_t\langle\psi| = \langle\psi|H^\dagger$. Start with $|\psi(t+\mathrm{d}t)\rangle = |\psi(t)\rangle - iH\mathrm{d}t|\psi(t)\rangle + \mathcal{O}((\mathrm{d}t)^2)$, which is equivalent to eq. (3.0.3). Then take the † on both sides to obtain $\langle\psi(t+\mathrm{d}t)| = \langle\psi(t)| + i\mathrm{d}t\langle\psi(t)|H^\dagger + \mathcal{O}((\mathrm{d}t)^2)$; the $\partial_t\langle\psi|$ can be defined as the coefficient of $\mathrm{d}t$.

On the other hand, if $H = H^\dagger$ then the time derivative of $\langle\psi|\,\psi\rangle$ must be zero.

Time Evolution Operator The time evolution operator U is the operator that obeys the Schrödinger equation

$$i\partial_t U(t,t') = HU(t,t') \tag{3.0.8}$$

and the boundary condition

$$U(t=t') = \mathbb{I}. \tag{3.0.9}$$

Suppose we were given some state of a system at time t', namely $|\psi(t')\rangle$. Then the same physical system at $t > t'$ can be gotten by acting U upon it:

$$|\psi(t)\rangle = U(t,t')\,|\psi(t')\rangle\,. \tag{3.0.10}$$

That eq. (3.0.10) solves Schrödinger's equation is because of eq. (3.0.8); while at $t = t'$, we utilize eq. (3.0.9) to check that $|\psi(t)\rangle \to |\psi(t')\rangle$ is recovered.

Problem 3.1. Prove the following properties of the time-evolution operator:

$$U(t_1,t_2)U(t_2,t_3) = U(t_1,t_3) \tag{3.0.11}$$

and

$$U(t_1,t_2)^\dagger = U(t_2,t_1); \tag{3.0.12}$$

where $t_{1,2,3}$ are arbitrary times. □

Time-independent Hamiltonians & Stationary States Whenever the Hamiltonian does not depend on time, the time evolution operator is simply

$$U(t,t') = \exp\left(-iH(t-t')\right). \tag{3.0.13}$$

It is easy to check that $e^{-iH(t-t')}$ satisfies both equations eq. (3.0.8) and (3.0.9). Under these circumstances, if a quantum system is found in an energy eigenstate $|E_n\rangle$ at time t', it will remain there for all times, since, according to eq. (3.0.10),

$$|\psi(t>t')\rangle = e^{-iH(t-t')}\,|E_n\rangle = e^{-iE_n(t-t')}\,|E_n\rangle\,. \tag{3.0.14}$$

3.1 Properties of Evolution Operators

In this section we will collect properties of evolution operators.

Definition Given some initial/fixed time t' and a Hermitian operator H – for our purposes here in this section, it does not necessarily need to be the Hamiltonian – the defining equation of the evolution operator U is

$$i\partial_t U[t,t'] = H[t]U[t,t'], \qquad U[t=t'] = \mathbb{I}. \tag{3.1.1}$$

We shall assume H does not depend on time derivatives; in particular, since this is a first order in time system, this means the solution to eq. (3.1.1) is unique. Taking the † on both sides also hands us:

$$i\partial_t U^\dagger[t,t'] = -U^\dagger[t,t']H[t], \qquad U^\dagger[t=t'] = \mathbb{I}. \tag{3.1.2}$$

Unitary The evolution operator defined by eq. (3.1.1) is unitary.

Proof We wish to show that $U^\dagger[t,t']U[t,t'] = \mathbb{I}$. Using eq. (3.1.1), i.e., $i\partial_t U = HU$ and $i\partial_t U^\dagger = -U^\dagger H$, we see that the time evolution of the LHS is governed by:

$$i\partial_t \left(U^\dagger[t,t']U[t,t']\right) = i\partial_t U^\dagger[t,t']U[t,t'] + U^\dagger[t,t']i\partial_t U[t,t'] \tag{3.1.3}$$

$$= -U^\dagger[t,t']H[t]U[t,t'] + U^\dagger[t,t']H[t]U[t,t'] = 0. \tag{3.1.4}$$

Therefore, $U^\dagger[t,t']U[t,t']$ is actually independent of t. To evaluate it for arbitrary t, therefore, we only need to do so at $t = t'$. The initial/boundary condition in eq. (3.1.1) says

$$U^\dagger[t=t']U[t=t'] = \mathbb{I}. \tag{3.1.5}$$

Solution I The (unique) solution to eq. (3.1.1) is

$$U[t,t'] = \mathbb{I} + \sum_{\ell=1}^{\infty}(-i)^\ell \int_{t'}^{t} \mathrm{d}t_\ell \int_{t'}^{t_\ell} \mathrm{d}t_{\ell-1} \cdots \int_{t'}^{t_3} \mathrm{d}t_2 \int_{t'}^{t_2} \mathrm{d}t_1 H[t_\ell]H[t_{\ell-1}]\ldots H[t_2]H[t_1]. \tag{3.1.6}$$

There is no restriction on whether $t \geq t'$ or $t < t'$ here.

Proof The initial condition $U[t=t'] = \mathbb{I}$ is obeyed. Therefore, we need only to check the differential equation – i.e., Schrödinger's equation – is satisfied:

$$\begin{aligned} i\partial_t U[t,t'] &= \sum_{\ell=1}^{\infty}(-i)^{\ell-1} H[t] \int_{t'}^{t} \mathrm{d}t_{\ell-1} \int_{t'}^{t_{\ell-1}} \mathrm{d}t_{\ell-2} \cdots \int_{t'}^{t_2} \mathrm{d}t_1 H[t_{\ell-1}]\ldots H[t_1] \\ &= H[t] \sum_{\ell=0}^{\infty}(-i)^{\ell} \int_{t'}^{t} \mathrm{d}t_{\ell} \int_{t'}^{t_{\ell}} \mathrm{d}t_{\ell-1} \cdots \int_{t'}^{t_2} \mathrm{d}t_1 H[t_{\ell}]\ldots H[t_1] \\ &= H[t]U[t,t'] \end{aligned}$$

Note that the zeroth ($\ell = 0$) term of the sum on the second line is $\mathbb{I}$.

Solution II The (unique) solution to eq. (3.1.1) can also be written as

$$U[t,t'] = \Theta_{\frac{1}{2}}[t-t']\mathsf{T}\left\{\exp\left[-i\int_{t'}^{t}\mathrm{d}t''H[t'']\right]\right\} + \Theta_{\frac{1}{2}}[t'-t]\overline{\mathsf{T}}\left\{\exp\left[i\int_{t}^{t'}\mathrm{d}t''H[t'']\right]\right\}, \tag{3.1.7}$$

where T denotes time ordering, i.e., every operator within the $\{\ldots\}$ is to be arranged such that operators evaluated at later times sit to the left of operators evaluated at earlier times. For example,

$$\mathsf{T}\{A[t_1]B[t_2]\} = \Theta_{\frac{1}{2}}[t_1-t_2]A[t_1]B[t_2] + \Theta_{\frac{1}{2}}[t_2-t_1]B[t_2]A[t_1],$$

and $\overline{\mathsf{T}}$ denotes anti time ordering, i.e., every operator within the $\{\dots\}$ is to be arranged such that operators evaluated at earlier times sit to the left of operators evaluated at later times. For example,

$$\overline{\mathsf{T}}\{A[t_1]B[t_2]\} = \Theta_{\frac{1}{2}}[t_2 - t_1]A[t_1]B[t_2] + \Theta_{\frac{1}{2}}[t_1 - t_2]B[t_2]A[t_1]. \tag{3.1.8}$$

Here the step function is defined as

$$\begin{aligned}
\Theta_{\frac{1}{2}}[t - t'] &= 1, \qquad \text{if } t > t' \\
\Theta_{\frac{1}{2}}[t - t'] &= 0, \qquad \text{if } t < t' \\
\Theta_{\frac{1}{2}}[t - t'] &= \frac{1}{2}, \qquad \text{if } t = t'.
\end{aligned}$$

Also the (anti) time ordered exponential(s) in eq. (3.1.7) is formal – they are really defined by its Taylor expansion:

$$\mathsf{T}\left\{\exp\left[-i\int_{t'}^{t} \mathrm{d}t''H[t'']\right]\right\} \equiv \mathsf{T}\left\{\mathbb{I} + \sum_{\ell=1}^{\infty}\frac{(-i)^\ell}{\ell!}\int_{t'}^{t}\mathrm{d}t_\ell\cdots\int_{t'}^{t}\mathrm{d}t_1 H[t_\ell]\dots H[t_1]\right\}, \qquad t \geq t', \tag{3.1.9}$$

and

$$\overline{\mathsf{T}}\left\{\exp\left[i\int_{t}^{t'} \mathrm{d}t''H[t'']\right]\right\} \equiv \overline{\mathsf{T}}\left\{\mathbb{I} + \sum_{\ell=1}^{\infty}\frac{i^\ell}{\ell!}\int_{t}^{t'}\mathrm{d}t_\ell\cdots\int_{t}^{t'}\mathrm{d}t_1 H[t_\ell]\dots H[t_1]\right\}, \qquad t < t'. \tag{3.1.10}$$

Proof Let us show that our solution for U satisfies eq. (3.1.1). The boundary condition $U[t = t'] = \mathbb{I}$ is manifest. We first note that T (applied to eq. (3.1.9)) commutes with both $\partial_{t'}$ and with ∂_t. This is because T does not involve either t nor t', since all the operators H are evaluated at the intermediate times t_1 through t_ℓ. Therefore we may deduce,

$$\begin{aligned}
i\partial_t U[t,t'] = \delta[t-t']\mathsf{T}\left\{\exp\left[-i\int_{t'}^{t}\mathrm{d}t''H[t'']\right]\right\} - \delta[t'-t]\overline{\mathsf{T}}\left\{\exp\left[i\int_{t}^{t'}\mathrm{d}t''H[t'']\right]\right\} \\
+ \Theta_{\frac{1}{2}}[t-t']\mathsf{T}\left\{i\partial_t\exp\left[-i\int_{t'}^{t}\mathrm{d}t''H[t'']\right]\right\} + \Theta_{\frac{1}{2}}[t'-t]\overline{\mathsf{T}}\left\{i\partial_t\exp\left[i\int_{t}^{t'}\mathrm{d}t''H[t'']\right]\right\}.
\end{aligned}$$

The derivatives of the two Θ-functions are each proportional to a δ-function, but one is negative of the other.[3] Therefore the terms on the RHS of the first line cancel. What remains is the differentiation of the exponentials. We have

$$\mathsf{T}\left\{i\partial_t\exp\left[-i\int_{t'}^{t}\mathrm{d}t''H[t'']\right]\right\}, \qquad t \geq t'$$

[3]We really have $\partial_z\Theta_{1/2}[z] = (1/2)\delta[z-0^+] + (1/2)\delta[z+0^+]$. To see this, we integrate from some $z = z_0 < 0$ to some arbitrary z. On both the LHS and RHS, if $z < 0$, the answer is zero. If $z = 0$, the LHS has to yield $1/2$, by definition; whereas on the RHS the integral picks up $1/2$ due to the non-trivial contribution from $\delta[z+0^+]$ and zero contribution from $\delta[z-0^+]$. Once $z > 0$, the LHS yields unity; while the RHS now receives a contribution of $1/2$ from each δ-function, thereby giving us unity. As far as the problem at hand is concerned, however, we can say $\delta[z-0^+] + \delta[z+0^+] = 2\delta[z]$. Our results here will probably not be affected if we had instead defined $\Theta[0] \equiv 1$.

$$= \mathsf{T}\left\{\sum_{\ell=1}^{\infty}\frac{(-i)^{\ell-1}}{\ell!}\sum_{s=1}^{\ell}\int_{t'}^{t}\mathrm{d}t_\ell\ldots\widehat{\int_{t'}^{t}\mathrm{d}t_s}\cdots\int_{t'}^{t}\mathrm{d}t_1 H[t_\ell]\ldots H[t_{s+1}]H[t]H[t_{s-1}]\ldots H[t_1]\right\}$$

$$= H[t]\mathsf{T}\left\{\sum_{\ell=1}^{\infty}\frac{(-i)^{\ell-1}}{\ell!}\sum_{s=1}^{\ell}\int_{t'}^{t}\mathrm{d}t_{\ell-1}\cdots\int_{t'}^{t}\mathrm{d}t_1 H[t_{\ell-1}]\ldots H[t_1]\right\}$$

$$= H[t]\mathsf{T}\left\{\sum_{\ell=1}^{\infty}\frac{(-i)^{\ell-1}}{(\ell-1)!}\int_{t'}^{t}\mathrm{d}t_{\ell-1}\cdots\int_{t'}^{t}\mathrm{d}t_1 H[t_{\ell-1}]\ldots H[t_1]\right\} \equiv H[t]\mathsf{T}\left\{\exp\left[-i\int_{t'}^{t}\mathrm{d}t'' H[t'']\right]\right\}.$$

The hat symbol indicates the t_s-integral is being omitted. On the second equality, we have re-labeled the integration variables to run from t_1 to $t_{\ell-1}$; and, we have pulled out $H[t]$ to the left of the time ordering operator, since t is the latest time. Note the subtlety in this calculation – because H is an operator, we cannot assume $H[t_i]$ and $H[t_j]$ commute if they are evaluated at different times; in particular,

$$i\partial_t \exp\left[-i\int_{t'}^{t}\mathrm{d}t'' H[t'']\right] \neq H[t]\exp\left[-i\int_{t'}^{t}\mathrm{d}t'' H[t'']\right]$$
$$i\partial_t \exp\left[-i\int_{t'}^{t}\mathrm{d}t'' H[t'']\right] \neq \exp\left[-i\int_{t'}^{t}\mathrm{d}t'' H[t'']\right] H[t].$$

It is the presence of the time ordering instruction that allows us to pull $H[t]$ all the way to the left. A similar calculation yields

$$\overline{\mathsf{T}}\left\{i\partial_t \exp\left[i\int_{t}^{t'}\mathrm{d}t'' H[t'']\right]\right\}, \qquad t < t'$$

$$= \overline{\mathsf{T}}\left\{\sum_{\ell=1}^{\infty}\frac{i^{\ell-1}}{\ell!}\sum_{s=1}^{\ell}\int_{t}^{t'}\mathrm{d}t_\ell\ldots\widehat{\int_{t}^{t'}\mathrm{d}t_s}\cdots\int_{t}^{t'}\mathrm{d}t_1 H[t_\ell]\ldots H[t_{s+1}](-i^2 H[t])H[t_{s-1}]\ldots H[t_1]\right\}$$

$$= H[t]\overline{\mathsf{T}}\left\{\sum_{\ell=1}^{\infty}\frac{i^{\ell-1}}{\ell!}\sum_{s=1}^{\ell}\int_{t}^{t'}\mathrm{d}t_{\ell-1}\cdots\int_{t}^{t'}\mathrm{d}t_1 H[t_{\ell-1}]\ldots H[t_1]\right\}$$

$$= H[t]\overline{\mathsf{T}}\left\{\sum_{\ell=1}^{\infty}\frac{i^{\ell-1}}{(\ell-1)!}\int_{t}^{t'}\mathrm{d}t_{\ell-1}\cdots\int_{t}^{t'}\mathrm{d}t_1 H[t_{\ell-1}]\ldots H[t_1]\right\} \equiv H[t]\overline{\mathsf{T}}\left\{\exp\left[i\int_{t}^{t'}\mathrm{d}t'' H[t'']\right]\right\}.$$

This means we have proven our solution for U satisfies eq. (3.1.1).

(Solution II)† We also have

$$U^\dagger[t,t'] = \Theta_{\frac{1}{2}}[t-t']\overline{\mathsf{T}}\left\{\exp\left[i\int_{t'}^{t}\mathrm{d}t'' H[t'']\right]\right\} + \Theta_{\frac{1}{2}}[t'-t]\mathsf{T}\left\{\exp\left[-i\int_{t}^{t'}\mathrm{d}t'' H[t'']\right]\right\}, \quad (3.1.11)$$

i.e.,

$$U^\dagger[t,t'] = U[t',t]. \quad (3.1.12)$$

Proof Simply take the Taylor series expansion in eq. (3.1.9) and take the † term by term.[4] First, $(-i)^\ell$ is replaced with i^ℓ and vice versa. Second, for some arbitrary positive integer s, if $t_s > t_{s-1} > \cdots > t_2 > t_1$, then

$$(H[t_s] \dots H[t_1])^\dagger = H[t_1] \dots H[t_s].$$

That is, a time ordered product of operators become an anti time ordered product. Taking the † on both sides once more shows an anti time ordered product of operators become a time ordered product.

Corollaries to Solution II The differential equation with respect to t' is

$$i\partial_{t'} U[t,t'] = -U[t,t']H[t']. \tag{3.1.13}$$

Therefore

$$i\partial_{t'} U^\dagger[t,t'] = H[t']U^\dagger[t,t']. \tag{3.1.14}$$

Notice these equations with respect to t' do not need to be imposed externally; they are a consequence of the defining equations with respect to t (i.e., eq. (3.1.1)).

Proof Let us prove eq. (3.1.13) via a direct calculation. We have,

$$\begin{aligned}
&\mathsf{T}\left\{ i\partial_{t'} \exp\left[-i\int_{t'}^{t} \mathrm{d}t'' H[t''] \right] \right\}, \qquad t \geq t' \\
&= \mathsf{T}\left\{ \sum_{\ell=1}^{\infty} \frac{(-i)^{\ell-1}}{\ell!} \sum_{s=1}^{\ell} \int_{t'}^{t} \mathrm{d}t_\ell \dots \widehat{\int_{t'}^{t} \mathrm{d}t_s} \cdots \int_{t'}^{t} \mathrm{d}t_1 H[t_\ell] \dots H[t_{s+1}](-H[t'])H[t_{s-1}] \dots H[t_1] \right\} \\
&= -\mathsf{T}\left\{ \sum_{\ell=1}^{\infty} \frac{(-i)^{\ell-1}}{\ell!} \sum_{s=1}^{\ell} \int_{t'}^{t} \mathrm{d}t_{\ell-1} \cdots \int_{t'}^{t} \mathrm{d}t_1 H[t_{\ell-1}] \dots H[t_1] \right\} H[t'] \\
&= -\mathsf{T}\left\{ \sum_{\ell=1}^{\infty} \frac{(-i)^{\ell-1}}{(\ell-1)!} \int_{t'}^{t} \mathrm{d}t_{\ell-1} \cdots \int_{t'}^{t} \mathrm{d}t_1 H[t_{\ell-1}] \dots H[t_1] \right\} H[t'] \equiv -\mathsf{T}\left\{ \exp\left[-i\int_{t'}^{t} \mathrm{d}t'' H[t''] \right] \right\} H[t'].
\end{aligned}$$

and

$$\begin{aligned}
&\overline{\mathsf{T}}\left\{ i\partial_{t'} \exp\left[i\int_{t}^{t'} \mathrm{d}t'' H[t''] \right] \right\}, \qquad t < t' \\
&= \overline{\mathsf{T}}\left\{ \sum_{\ell=1}^{\infty} \frac{i^{\ell-1}}{\ell!} \sum_{s=1}^{\ell} \int_{t}^{t'} \mathrm{d}t_\ell \dots \widehat{\int_{t}^{t'} \mathrm{d}t_s} \cdots \int_{t}^{t'} \mathrm{d}t_1 H[t_\ell] \dots H[t_{s+1}](i^2 H[t'])H[t_{s-1}] \dots H[t_1] \right\} \\
&= -\overline{\mathsf{T}}\left\{ \sum_{\ell=1}^{\infty} \frac{i^{\ell-1}}{\ell!} \sum_{s=1}^{\ell} \int_{t}^{t'} \mathrm{d}t_{\ell-1} \cdots \int_{t}^{t'} \mathrm{d}t_1 H[t_{\ell-1}] \dots H[t_1] \right\} H[t'] \\
&= -\overline{\mathsf{T}}\left\{ \sum_{\ell=1}^{\infty} \frac{i^{\ell-1}}{(\ell-1)!} \int_{t}^{t'} \mathrm{d}t_{\ell-1} \cdots \int_{t}^{t'} \mathrm{d}t_1 H[t_{\ell-1}] \dots H[t_1] \right\} H[t'] \equiv -\overline{\mathsf{T}}\left\{ \exp\left[i\int_{t}^{t'} \mathrm{d}t'' H[t''] \right] \right\} H[t'].
\end{aligned}$$

[4]Note: as long as the (anti) time ordered symbol is in place, the order of the operators within the $\{\dots\}$ is immaterial.

A much simpler proof would be to start from the Schrödinger equation $i\partial_t U[t,t'] = HU[t,t']$, take the dagger on both sides, and employing eq. (3.1.12).

$$-i\partial_t U^\dagger[t,t'] = U^\dagger[t,t']H, \tag{3.1.15}$$
$$-i\partial_t U[t',t] = U[t',t]H. \tag{3.1.16}$$

Group property The evolution operator obeys

$$U[t,t'']U[t'',t'] = U[t,t'], \tag{3.1.17}$$

with no restriction on the relative chronologies of t, t' and t''.

Proof We have to show that both sides obey the defining equations in eq. (3.1.1). It is manifest that $i\partial_t U = HU$ is obeyed and, as $t \to t'$, the RHS tends to $\mathbb{I}$. Thus, we merely have to check the boundary condition that $U[t,t'']U[t'',t']$ tends to the identity when $t \to t'$: namely, $U[t',t'']U[t'',t'] = U^\dagger[t'',t']U[t'',t'] = \mathbb{I}$, where eq. (3.1.12) was used in the first equality and the unitary property of U was employed in the second equality.

Operator insertion If we insert an operator Q in eq. (3.1.17):

$$\begin{aligned} &U[t,t']Q[t']U[t',t] = U^\dagger[t',t]Q[t']U[t',t] = U[t,t']Q[t']U^\dagger[t,t'] \\ &= Q[t'] + \sum_{\ell=1}^{\infty}(-i)^\ell \int_{t'}^{t} \mathrm{d}t_\ell \int_{t'}^{t_\ell} \mathrm{d}t_{\ell-1} \cdots \int_{t'}^{t_3} \mathrm{d}t_2 \int_{t'}^{t_2} \mathrm{d}t_1 \\ &\qquad \times \Big[H[t_\ell], \Big[H[t_{\ell-1}], \Big[\dots \Big[H[t_2], \Big[H[t_1], Q[t']\Big]\Big] \dots \Big]\Big]\Big]. \end{aligned}$$

Proof As $t \to t'$ we have the boundary condition $U[t,t']Q[t']U[t',t] \to Q[t']$. This is obeyed on the RHS too. We may now check that both the LHS and RHS obeys the same first order in time differential equation with respect to t. Differentiating LHS yields

$$\begin{aligned} i\partial_t \left(U[t,t']Q[t']U^\dagger[t,t']\right) &= H[t]U[t,t']Q[t']U^\dagger[t,t'] - U[t,t']Q[t']U^\dagger[t,t']H[t] \\ &\equiv \Big[H[t], U[t,t']Q[t']U^\dagger[t,t']\Big]. \end{aligned}$$

Denote

$$\mathcal{R}[t,t'] \equiv Q[t'] + \sum_{\ell=1}^{\infty}(-i)^\ell \int_{t'}^{t} \mathrm{d}t_\ell \int_{t'}^{t_\ell} \mathrm{d}t_{\ell-1} \cdots \int_{t'}^{t_3} \mathrm{d}t_2 \int_{t'}^{t_2} \mathrm{d}t_1 \Big[H[t_\ell], \Big[H[t_{\ell-1}], \Big[\dots \Big[H[t_1], Q[t']\Big] \dots \Big]\Big]\Big].$$

Differentiating the RHS gives us

$$\begin{aligned} i\partial_t \mathcal{R}[t,t'] &= \sum_{\ell=1}^{\infty}(-i)^{\ell-1} \Big[H[t], \int_{t'}^{t} \mathrm{d}t_{\ell-1} \int_{t'}^{t_{\ell-1}} \mathrm{d}t_{\ell-2} \cdots \int_{t'}^{t_3} \mathrm{d}t_2 \int_{t'}^{t_2} \mathrm{d}t_1 \Big[H[t_{\ell-1}], \Big[\dots \Big[H[t_1], Q[t']\Big] \dots \Big]\Big]\Big] \\ &= \Big[H[t], \mathcal{R}[t,t']\Big]. \end{aligned} \tag{3.1.18}$$

4 Heisenberg & Schrödinger Pictures: Time-Independent Hamiltonian

Just as choosing the right coordinates is often an important step in simplifying a given problem, the choice of the right basis in a given quantum mechanical problem can often provide the crucial insights. Moreover, recall that the change-of-basis between two orthonormal basis is implemented via a unitary transformation. In this section we will study the change-of-basis related to time-evolution itself, in the case where the Hamiltonian H is time-independent.

Schrödinger Picture If $|\psi(t)\rangle$ describes the physical state of a quantum system, the Schrödinger picture is defined as the basis where the Schrödinger equation is obeyed:

$$i\partial_t |\psi(t)\rangle = H |\psi(t)\rangle . \tag{4.0.1}$$

If $|\psi(t_0)\rangle$ is the state at time t_0, you may verify through a direct calculation the solution to $|\psi(t > t_0)\rangle$ is given by

$$|\psi(t \geq t_0)\rangle = U(t, t_0) |\psi(t_0)\rangle , \tag{4.0.2}$$

$$U(t, t') \equiv \exp\left(-iH(t - t')\right), \qquad U(t = t') = \mathbb{I}. \tag{4.0.3}$$

Eigen-spectrum Within the Schrödinger picture, the position, momentum and angular momentum operators do not depend on time; and their eigenstates and values also do not depend on time. This statement also holds for any other time-independent observable A.

$$A |a\rangle = a |a\rangle \qquad : \qquad \partial_t |a\rangle = 0 \qquad \text{if} \qquad \partial_t A = 0. \tag{4.0.4}$$

If an observable A does not commute with the Hamiltonian H, then in general if a system at time t_0 is found in one of its eigenstates $|a\rangle$, at a late time $t > t_0$ it will no longer be the same eigenstate. From eq. (4.0.2),

$$|\psi(t > t_0)\rangle = e^{-iH(t-t_0)} |a\rangle \tag{4.0.5}$$

is usually *not* proportional to $|a\rangle$ itself, for arbitrary $|a\rangle$, for it were then $e^{-iH(t-t_0)} |a\rangle = \lambda_a |a\rangle$ (for some eigenvalue λ_a) would be a simultaneous eigenket of both $\exp(-iH(t - t_0))$ and A and thus $[H, A] = 0$.

Heisenberg Picture The Heisenberg picture is usually defined using its relation to the Schrödinger picture. There is also a need to choose some time t_0 where the two pictures coincide.

The motivation goes as follows, suppose $|\psi(t)\rangle$ is a physical state in the Schrödinger picture and O is some (not necessarily Hermitian) time-independent operator. The time-dependent expectation value of O with respect to this physical state is

$$\langle\psi(t)| O |\psi(t)\rangle . \tag{4.0.6}$$

But using eq. (4.0.2),

$$\langle\psi(t)| O |\psi(t)\rangle = \langle\psi(t_0)| U(t, t_0)^\dagger O U(t, t_0) |\psi(t_0)\rangle . \tag{4.0.7}$$

Within the Heisenberg picture, physical states $\{|\psi\rangle_{\rm H}\}$ are defined to be the $\{\psi(t_0)\}$ within the Schrödinger picture at time t_0, namely

$$|\psi\rangle_{\rm H} \equiv |\psi(t_0)\rangle\,, \tag{4.0.8}$$

and are therefore time-independent.

Linear operators $\{O_{\rm H}(t)\}$ in the Heisenberg picture are related to those in the Schrödinger picture $\{O\}$ through the change-of-basis implemented by the time evolution operator itself (cf. eq. (4.0.3)). Since U depends on time, this implies $O_{\rm H}$ typically depends on time too:

$$O_{\rm H}(t) \equiv U(t,t_0)^\dagger O U(t,t_0). \tag{4.0.9}$$

An exception occurs whenever O commutes with H. For instance, whenever H is time-independent, it commutes with itself for all times, and therefore

$$U^\dagger(t,t_0) H U(t,t_0) = e^{+iH(t-t_0)} H e^{-iH(t-t_0)} = e^{+iH(t-t_0)} e^{-iH(t-t_0)} H = H. \tag{4.0.10}$$

We highlight this important exception.

> Whenever the Hamiltonian H is time independent, it takes the same form in both the Heisenberg and Schrödinger pictures.

Returning to the defining Heisenberg picture equations (4.0.8) and (4.0.9), we see that eq. (4.0.7) may now be written as

$$\langle\psi(t)\,|O|\,\psi(t)\rangle = {}_{\rm H}\langle\psi\,|O_{\rm H}(t)|\,\psi\rangle_{\rm H}\,. \tag{4.0.11}$$

Eigen-spectrum Within the Heisenberg picture, eq. (4.0.9) tells us that observables are generically time-dependent. For example, whenever the position $\vec{X}$, momentum $\vec{P}$, and/or angular momentum operators $\vec{J}$ do not commute with the Hamiltonian H, they become time-dependent in the Heisenberg picture.

$$\vec{X}_{\rm H}(t) = U(t,t_0)^\dagger \vec{X} U(t,t_0), \tag{4.0.12}$$

$$\vec{P}_{\rm H}(t) = U(t,t_0)^\dagger \vec{P} U(t,t_0), \tag{4.0.13}$$

$$\vec{J}_{\rm H}(t) = U(t,t_0)^\dagger \vec{J} U(t,t_0). \tag{4.0.14}$$

This in turn implies, since observables $\{A\}$ are generically time-dependent, their eigen-states become generically time dependent too:

$$A_{\rm H}(t)\,|a,t\rangle_{\rm H} = a\,|a,t\rangle_{\rm H}\,. \tag{4.0.15}$$

Problem 4.1. Equations-of-Motion Whenever O does not commute with H, then computing $U^\dagger O U$ may not be easy.[5] An alternate perspective is to tackle the following first order equation. Prove that

$$\dot{O}_{\rm H}(t) = i\,[H, O_{\rm H}(t)]\,. \tag{4.0.16}$$

[5] One may always write down an infinite series expansion using the Baker-Campbell-Hausdorff lemma.

If $\vec{X}_{\rm H}$, $\vec{P}_{\rm H}$ and $\vec{J}_{\rm H}$ are the position, momentum and orbitary angular momentum operators of the simple harmonic oscillator with Hamiltonian

$$H = \frac{1}{2}\vec{P}^2 + \frac{\omega^2}{2}\vec{X}^2, \tag{4.0.17}$$

solve them in terms of their Schrödinger counterparts $\vec{X}$, $\vec{P}$ and $\vec{J}$. □

Ehrenfest Theorem Suppose the Hamiltonian is the usual kinetic plus potential energy, namely

$$H = \frac{\vec{P}^2}{2m} + V(\vec{X}). \tag{4.0.18}$$

We will now see that Newton's second law is recovered at the operator level, namely

$$m\ddot{\vec{X}}_{\rm H} = -\vec{\nabla}V(\vec{X}_{\rm H}). \tag{4.0.19}$$

To see this, we simply employ eq. (4.0.16) and

$$\left[X^i_{(s)}, P_{(s)_j}\right] = i\delta^i_j \qquad \Leftrightarrow \qquad U(t,t_0)^\dagger \left[X^i_{(s)}, P_{(s)_j}\right] U(t,t_0) = \left[X^i_{({\rm H})}, P_{({\rm H})_j}\right] = i\delta^i_j. \tag{4.0.20}$$

Suppressing the subscript H, but working in the Heisenberg picture – the second derivative reads

$$\begin{aligned}
\ddot{X}^i = i\left[H, \dot{X}^i\right] &= i^2\left[H, \left[H, X^i\right]\right] \\
&= -\left[\frac{\vec{P}^2}{2m} + V, \left[\frac{\vec{P}^2}{2m}, X^i\right]\right] = -(2m)^{-1}\left[\frac{\vec{P}^2}{2m} + V, P_j\left[P_j, X^i\right] + \left[P_j, X^i\right]P_j\right] \\
&= im^{-1}\left[V(\vec{X}), P_i\right] \qquad (4.0.21) \\
\ddot{\vec{X}} &= -m^{-1}\vec{\nabla}V(\vec{X}). \qquad (4.0.22)
\end{aligned}$$

Problem 4.2. Anti-Time-Evolution If at arbitrary time t, the $|a,t\rangle_{\rm H}$ is an eigenstate of the observable $A_{\rm H}(t)$, show that

$$|a,t\rangle_{\rm H} = U(t,t_0)^\dagger |a\rangle . \tag{4.0.23}$$

Namely, eigenkets in the Heisenberg picture are the anti-time-evolved Schrödinger picture ones. Explain why the eigenvalues do not depend on time, as long as the operator A in the Schrödinger picture is time-independent. □

The completeness relation of observables $\{A\}$ in the Schrödinger picture reads

$$\sum_a |a\rangle\langle a| = \mathbb{I}, \qquad\qquad A|a\rangle = a|a\rangle . \tag{4.0.24}$$

In the Heisenberg picture, they read

$$\sum_a |a,t\rangle_{\rm H}\ {}_{\rm H}\langle a,t| = \mathbb{I}, \qquad\qquad A_{\rm H}(t)|a,t\rangle_{\rm H} = a|a,t\rangle_{\rm H} . \tag{4.0.25}$$

For instance, if $\vec{X}$ is the position operator and $\vec{x}$ is its eigenket,

$$\int \mathrm{d}^D\vec{x}\,|\vec{x},t\rangle_{\mathrm{H}}\ {}_{\mathrm{H}}\langle\vec{x},t| = \mathbb{I}. \tag{4.0.26}$$

To demonstrate the validity of eq. (4.0.25), we employ eq. (4.0.23) followed by the completeness relation in the Schrödinger picture.

$$\sum_a |a,t\rangle_{\mathrm{H}}\ {}_{\mathrm{H}}\langle a,t| = U(t,t_0)^\dagger \sum_a |a\rangle\langle a|\,U(t,t_0) = U(t,t_0)^\dagger\mathbb{I}U(t,t_0) = \mathbb{I}. \tag{4.0.27}$$

Of course, we could also simply recognize eq. (4.0.9), with $O = A$ here, as being a change-of-basis, which does not affect the Hermitian character of the operator in question.

Problem 4.3. Show that

$${}_{\mathrm{H}}\langle\vec{x},t|\,a,t\rangle_{\mathrm{H}} = \langle\vec{x}|\,a\rangle\,. \tag{4.0.28}$$

That is, the position-representation of some eigenket of an observable is picture-independent. □

Problem 4.4. Energy Eigenket Expectation Value Explain why

$$\langle E\,|O|\,E\rangle = {}_{\mathrm{H}}\langle E,t_\star\,|O_{\mathrm{H}}(t)|\,E,t_\star\rangle_{\mathrm{H}}\,, \tag{4.0.29}$$

where $t_\star$ is an arbitrary time. In the Schrödinger picture, recall that, if the physical system is in the energy eigenstate $|\psi(t_0)\rangle = |E\rangle$, then $\langle\psi(t)\,|O|\,\psi(t)\rangle = \langle E\,|O|\,E\rangle$; i.e., the time t in $|\psi(t)\rangle$ is immaterial. This result in eq. (4.0.29) tells us the same statement holds in the Heisenberg picture. □

5 Interaction Picture & Time Evolution

Motivation In many situations, the Hamiltonian H is the sum of an exactly solvable (or, at least, well understood) H_0 and a complicated but 'small' perturbation H'.

$$H = H_0 + H'(t) \tag{5.0.1}$$

For instance, H_0 might describe the hydrogen atom and H' its interaction with an externally applied electromagnetic field. We shall see how the interaction picture allows us to re-write Schrödinger's equation in such a way to implement time evolution as a perturbation theory in powers of H'.

The interpretation will be as follows. We shall assume H' is weak enough, so that the eigenstates of H_0 can still be treated as the possible outcomes of physical experiments. Hence, the primary question is – with the passage of time – how does H' drive transitions between the eigenstates of H_0?

Time Evolution We will define the interaction picture in terms of the Schrödinger picture. Denoting the former by the subscript 'I' and the latter by 's', physical states are related via

$$\left|\psi(t)\right\rangle_{\mathrm{I}} = U_0^\dagger \left|\psi(t)\right\rangle_{\mathrm{s}}, \tag{5.0.2}$$

where U_0 is the time evolution operator corresponding to H_0, namely

$$i\partial_t U_0(t,t_0) = H_0 U_0(t,t_0) \qquad \text{and} \qquad U_0(t=t_0) = \mathbb{I}. \tag{5.0.3}$$

Referring to eq. (5.0.2), the t_0 is therefore the time where the Schrödinger and interaction pictures coincide.

The linear operators are related via

$$O_{\mathrm{I}} = U_0^\dagger O_{\mathrm{s}} U_0. \tag{5.0.4}$$

This is to preserve the form of the matrix element between arbitrary states $|\psi_{1,2}\rangle$:

$$\begin{aligned} {}_{\mathrm{I}}\left\langle\psi_1(t)\right|O_{\mathrm{I}}\left|\psi_2(t)\right\rangle_{\mathrm{I}} &= {}_{\mathrm{s}}\left\langle\psi_1(t)\right|U_0 U_0^\dagger O_{\mathrm{s}} U_0 U_0^\dagger\left|\psi_2(t)\right\rangle_{\mathrm{s}} && (5.0.5)\\ &= {}_{\mathrm{s}}\left\langle\psi_1(t)\right|O_{\mathrm{s}}\left|\psi_2(t)\right\rangle_{\mathrm{s}}. && (5.0.6)\end{aligned}$$

The eigenkets $\{|a;t\rangle_{\mathrm{I}}\}$ of an observable A_{I} within the interaction picture are related to its Schrödinger picture counterparts $\{|a;t\rangle_{\mathrm{s}}\}$ of an observable A_{s} through

$$\left|a;t\right\rangle_{\mathrm{I}} = U_0(t,t_0)^\dagger \left|a\right\rangle_{\mathrm{s}}; \tag{5.0.7}$$

because

$$\begin{aligned} A_{\mathrm{I}}\left|a;t\right\rangle_{\mathrm{I}} &= U_0^\dagger A_{\mathrm{s}} U_0 U_0^\dagger \left|a\right\rangle_{\mathrm{s}} && (5.0.8)\\ &= U_0^\dagger A_{\mathrm{s}}\left|a\right\rangle_{\mathrm{s}} = a\cdot U_0^\dagger\left|a\right\rangle_{\mathrm{s}} && (5.0.9)\\ &= a\left|a;t\right\rangle_{\mathrm{I}}. && (5.0.10)\end{aligned}$$

Let us examine the time evolution of an interaction picture state. If, within the Schrödinger picture,

$$i\partial_t U(t,t') = HU(t,t') = (H_0 + H')U(t,t') \qquad \text{and} \qquad U(t=t') = \mathbb{I}; \tag{5.0.11}$$

then according to eq. (5.0.2),

$$|\psi(t)\rangle_{\rm I} = U_{\rm I}(t,t_0)\,|\psi(t_0)\rangle_{\rm s}\,, \tag{5.0.12}$$

$$U_{\rm I}(t,t_0) \equiv U_0(t,t_0)^\dagger U(t,t_0). \tag{5.0.13}$$

This $U_{\rm I}$ is *not* the Schrödinger picture U re-expressed in interaction picture,[6] but we are abusing notation somewhat for technical convenience. In any case, $U_{\rm I}$ does take a Schrödinger picture initial state and evolves it to an interaction picture state at time t. What is important is its equations-of-motion.

$$i\dot{U}_{\rm I} = -(i\dot{U}_0)^\dagger U + U_0(i\dot{U}) \tag{5.0.14}$$

$$= U_0^\dagger(-H_0)U + U_0 H U \tag{5.0.15}$$

$$= U_0^\dagger(-H_0 + H_0 + H')U = U_0^\dagger H' U_0 U_0^\dagger U \tag{5.0.16}$$

$$= H'_{\rm I} U_{\rm I}. \tag{5.0.17}$$

In words: the $U_{\rm I}$ obeys the Schrödinger equation, but with respect to the Hamiltonian $H'_{\rm I}$ written in the interaction picture.

Operator Equation Admitting Dyson Series As Solution Consider the operator equation

$$\dot{A} = BA, \tag{5.0.18}$$

where the overdot denotes time derivative, and both A and B are operators. The solution is the Dyson series

$$A(t) = \left(\mathbb{I} + \sum_{\ell=1}^{+\infty} \int_{t_0}^{t} \mathrm{d}s_\ell \int_{t_0}^{s_\ell} \mathrm{d}s_{\ell-1} \cdots \int_{t_0}^{s_3} \mathrm{d}s_2 \int_{t_0}^{s_2} \mathrm{d}s_1 B(s_\ell)B(s_{\ell-1})\ldots B(s_2)B(s_1)\right) A(t_0). \tag{5.0.19}$$

Note that the ordering of these Bs and $A(t_0)$ are important, because they are operators. From eq. (5.0.14) and the initial condition $U_{\rm I}(t=t_0) = \mathbb{I}$, we may therefore solve the $U_{\rm I}$ solely in terms of $H'_{\rm I}$.

$$U_{\rm I}(t,t_0) = \left(\mathbb{I} + \sum_{\ell=1}^{+\infty} (-i)^\ell \int_{t_0}^{t} \mathrm{d}s_\ell \int_{t_0}^{s_\ell} \mathrm{d}s_{\ell-1} \cdots \int_{t_0}^{s_3} \mathrm{d}s_2 \int_{t_0}^{s_2} \mathrm{d}s_1 H'_{\rm I}(s_\ell)H'_{\rm I}(s_{\ell-1})\ldots H'_{\rm I}(s_2)H'_{\rm I}(s_1)\right). \tag{5.0.20}$$

[6] The interaction picture evolution operator, namely $U_0^\dagger(t,t_0)U(t,t_0)U_0(t,t_0)$, does not in fact evolve the initial state properly – i.e., $|\psi(t)\rangle_{\rm I} \neq U_0^\dagger(t,t_0)U(t,t_0)U_0(t,t_0)\,|\psi(t_0)\rangle_{\rm I}$ – because the state it acts on (namely, $|\psi(t_0)\rangle_{\rm I} = |\psi(t_0)\rangle_{\rm s}$) is not evaluated at the same time as the operator itself.

Time-Dependent Perturbation Theory We will assume H_0 is a time-independent Hermitian operator; whereas H' is a time-dependent one. As we shall witness, the interaction picture physical ket may therefore be solved in terms of the eigenkets of H_0, which obey

$$H_0 \left|\bar{E}_n\right\rangle_{\mathrm{s}} = \bar{E}_n \left|\bar{E}_n\right\rangle_{\mathrm{s}}. \tag{5.0.21}$$

From eq. (5.0.7) and the time-independence of the H_0 to recall $U_0(t,t_0) = \exp(-iH_0(t-t_0))$,

$$\left|\bar{E}_n;t\right\rangle_{\mathrm{I}} = e^{i\bar{E}_n(t-t_0)}\left|\bar{E}_n\right\rangle_{\mathrm{s}} = U_0(t,t_0)^\dagger \left|\bar{E}_n\right\rangle_{\mathrm{s}}. \tag{5.0.22}$$

The solution, according to eq. (5.0.20) inserted into eq. (5.0.12), is

$$\begin{aligned}&|\psi(t)\rangle_{\mathrm{I}} = U_{\mathrm{I}}(t,t_0)\,|\psi(t_0)\rangle_{\mathrm{s}} \qquad (5.0.23)\\ &= \left(\mathbb{I} + \sum_{\ell=1}^{+\infty}(-i)^\ell \int_{t_0}^{t} \mathrm{d}s_\ell \int_{t_0}^{s_\ell} \mathrm{d}s_{\ell-1}\cdots \int_{t_0}^{s_3} \mathrm{d}s_2 \int_{t_0}^{s_2} \mathrm{d}s_1 H'_{\mathrm{I}}(s_\ell)H'_{\mathrm{I}}(s_{\ell-1})\ldots H'_{\mathrm{I}}(s_2)H'_{\mathrm{I}}(s_1)\right)|\psi(t_0)\rangle_{\mathrm{s}}.\end{aligned}$$

Employing eq. (5.0.7)

$$U_0\,|a;t\rangle_{\mathrm{I}} = |a\rangle_{\mathrm{s}} \qquad \text{and} \qquad {}_{\mathrm{I}}\langle a;t| = {}_{\mathrm{s}}\langle a|\,U_0; \tag{5.0.24}$$

as well as $|\psi(t)\rangle_{\mathrm{s}} = U(t,t_0)\,|\psi(t_0)\rangle$, the quantum amplitude for finding the physical system in the eigenstate $\left|\bar{E}_n\right\rangle$ at time t is given by

$$\begin{aligned}{}_{\mathrm{s}}\left\langle \bar{E}_n\right|\psi(t)\rangle_{\mathrm{s}} &= {}_{\mathrm{s}}\left\langle \bar{E}_n\right|U_0(t,t_0)U_0(t,t_0)^\dagger U(t,t_0)\left|\psi(t_0)\right\rangle_{\mathrm{s}} &(5.0.25)\\ &= e^{-i\bar{E}_n(t-t_0)}\,{}_{\mathrm{s}}\left\langle \bar{E}_n\right|U_{\mathrm{I}}(t,t_0)\left|\psi(t_0)\right\rangle_{\mathrm{s}}. &(5.0.26)\end{aligned}$$

The probability that the quantum will be found in the state $\left|\bar{E}_n\right\rangle_{\mathrm{s}}$ at time $t > t_0$ is given by

$$P\left(t_0, |\psi_0\rangle \to t, \left|\bar{E}_n\right\rangle\right) = |c_n(t)|^2; \tag{5.0.27}$$

where, following Weinberg, we have defined

$$\begin{aligned}c_n(t) &\equiv {}_{\mathrm{s}}\left\langle \bar{E}_n\right|U_{\mathrm{I}}(t,t_0)\left|\psi(t_0)\right\rangle_{\mathrm{s}}\\ &= e^{i\bar{E}_n(t-t_0)}\,{}_{\mathrm{s}}\left\langle \bar{E}_n\right|\psi(t)\rangle_{\mathrm{s}}. &(5.0.28)\end{aligned}$$

Moreover the physical state itself can now be expressed as

$$\begin{aligned}|\psi(t)\rangle_{\mathrm{s}} &= \sum_\ell \left|\bar{E}_\ell\right\rangle_{\mathrm{s}}\,{}_{\mathrm{s}}\left\langle \bar{E}_\ell\right|\psi(t)\rangle_{\mathrm{s}} &(5.0.29)\\ &= \sum_\ell e^{-i\bar{E}_\ell(t-t_0)}c_\ell(t)\left|\bar{E}_\ell\right\rangle. &(5.0.30)\end{aligned}$$

Since we know the differential equation for U_{I}, we may readily obtain one for $c_n(t)$.

$$\begin{aligned}i\partial_t c_n(t) &= {}_{\mathrm{s}}\left\langle \bar{E}_n\right|H'_{\mathrm{I}}(t)U_{\mathrm{I}}(t,t_0)\left|\psi(t_0)\right\rangle_{\mathrm{s}} &(5.0.31)\\ &= {}_{\mathrm{s}}\left\langle \bar{E}_n\right|U_0^\dagger H'(t)U_0U_{\mathrm{I}}(t,t_0)\left|\psi(t_0)\right\rangle_{\mathrm{s}} &(5.0.32)\end{aligned}$$

$$= {}_{\rm s}\left\langle \bar{E}_n \right| e^{i\bar{E}_n(t-t_0)} H'_{\rm s}(t) e^{-iH_0(t-t_0)} \sum_\ell \left| \bar{E}_\ell \right\rangle_{\rm s} {}_{\rm s}\left\langle \bar{E}_\ell \right| U_{\rm I}(t,t_0) \left|\psi(t_0)\right\rangle_{\rm s} . \tag{5.0.33}$$

We arrive at

$$i\partial_t c_n(t) = H'_{n\ell}(t) c_\ell(t), \tag{5.0.34}$$

$$\begin{aligned} H'_{n\ell}(t) &\equiv e^{i(\bar{E}_n - \bar{E}_\ell)(t-t_0)} {}_{\rm s}\left\langle \bar{E}_n \right| H'_{\rm s}(t) \left| \bar{E}_\ell \right\rangle_{\rm s} \\ &= {}_{\rm I}\left\langle \bar{E}_n, t \right| H'_{\rm s}(t) \left| \bar{E}_\ell, t \right\rangle_{\rm I} . \end{aligned} \tag{5.0.35}$$

First Order Time-Dependent PT To first order in $H'_{\rm I}$, we may employ eq. (5.0.23) to deduce the quantum transition amplitude is

$$c_n(t) = {}_{\rm s}\left\langle \bar{E}_n \right| \mathbb{I} - i \int_{t_0}^t H'_{\rm I}(s) {\rm d}s + \ldots \left|\psi(t_0)\right\rangle . \tag{5.0.36}$$

In particular, if the physical system began at some eigenstate of H_0, say

$$\left|\psi(t_0)\right\rangle = \left| \bar{E}_a \right\rangle_{\rm s} ; \tag{5.0.37}$$

then we see that the transition amplitude $\mathcal{M}(\bar{E}_a \to \vec{E}_b)$ is provided by the expression

$$\mathcal{M}(\bar{E}_a \to \vec{E}_b) \equiv e^{i\bar{E}_b(t-t_0)} {}_{\rm s}\left\langle \bar{E}_b \right| \psi(t) \left\rangle_{\rm s} \right. \tag{5.0.38}$$

$$= \delta^b_a - i \int_{t_0}^t {}_{\rm s}\left\langle \bar{E}_b \left| U_0^\dagger H'_{\rm s}(\tau) U_0 \right| \bar{E}_a \right\rangle_{\rm s} {\rm d}\tau + \ldots \tag{5.0.39}$$

$$= \delta^b_a - i \int_{t_0}^t e^{i(\bar{E}_b - \bar{E}_a)(s-t_0)} {}_{\rm s}\left\langle \bar{E}_b \left| H'_{\rm s}(\tau) \right| \bar{E}_a \right\rangle_{\rm s} {\rm d}\tau + \ldots \tag{5.0.40}$$

If, furthermore, we are interested in nontrivial transitions ($b \neq a$); then the probability of such a process is – up to first order in perturbation theory – given by

$$\left| \mathcal{M}\left(\bar{E}_a \to \vec{E}_b; {}^{b\neq a}_{t_0 \to t} \right) \right|^2 \approx \left| \int_{t_0}^t e^{i(\bar{E}_b - \bar{E}_a)s} {}_{\rm s}\left\langle \bar{E}_b \left| H'_{\rm s}(\tau) \right| \bar{E}_a \right\rangle_{\rm s} {\rm d}\tau \right|^2 . \tag{5.0.41}$$

Constant Perturbation & Fermi's Golden Rule version I We start with a constant perturbation V that is turned on after $t > 0$; namely,

$$H_s(s < 0) = 0, \tag{5.0.42}$$

$$H_s(s \geq 0) = V \qquad \text{(time-independent)}. \tag{5.0.43}$$

To first order, we evaluate

$$\mathcal{M}\left(\bar{E}_a \to \vec{E}_b; {}^{b\neq a}_{t_0 \to t} \right) = \int_{t_0}^t e^{i(\bar{E}_b - \bar{E}_a)s} {}_{\rm s}\left\langle \bar{E}_b \left| H'_{\rm s}(s) \right| \bar{E}_a \right\rangle_{\rm s} \tag{5.0.44}$$

$$= V_{ba} \int_{t_0}^t e^{i(\bar{E}_b - \bar{E}_a)s} \Theta(s) {\rm d}s \tag{5.0.45}$$

$$V_{ba} \equiv {}_{\rm s}\left\langle \bar{E}_b \right| V \left| \bar{E}_a \right\rangle_{\rm s} . \tag{5.0.46}$$

As long as the initial time t_0 is negative, it does not matter what its actual numerical value is. Moreover, for $t_0 < t < 0$, the amplitude is zero since $H' = 0$. Hence, the amplitude is proportional to $\Theta(t)$.

$$\mathcal{M}\left(\bar{E}_a \to \vec{E}_b; {}^{b\neq a}_{t_0\to t}\right) = \Theta(t)\ V_{ba}\frac{e^{i(\bar{E}_b-\bar{E}_a)t}-1}{i(\bar{E}_b-\bar{E}_a)} \tag{5.0.47}$$

$$= \Theta(t)\ V_{ba}e^{i(\bar{E}_b-\bar{E}_a)t/2}\frac{e^{i(\bar{E}_b-\bar{E}_a)t/2}-e^{-i(\bar{E}_b-\bar{E}_a)t/2}}{i(\bar{E}_b-\bar{E}_a)} \tag{5.0.48}$$

$$= \Theta(t)\ V_{ba}e^{i(\bar{E}_b-\bar{E}_a)t/2}\frac{2\sin\left((\bar{E}_b-\bar{E}_a)t/2\right)}{\bar{E}_b-\bar{E}_a}. \tag{5.0.49}$$

Because $\Theta(t)^2 = \Theta(t)$, we have

$$\left|\mathcal{M}\left(\bar{E}_a \to \vec{E}_b; {}^{b\neq a}_{t_0\to t}\right)\right|^2 = \Theta(t)|V_{ba}|^2t^2\left(\frac{\sin\left((\bar{E}_b-\bar{E}_a)t/2\right)}{(\bar{E}_b-\bar{E}_a)t/2}\right)^2. \tag{5.0.50}$$

This $(\sin(\Delta E\cdot t/2)/(\Delta E\cdot t/2))^2$ becomes more and more sharply peaked around the origin $\Delta E\cdot t/2 \approx 0$ as $t\to\infty$. Suppose we ask, what is the number of ways that the quantum system can transition from $\bar{E}_a$ to a 'region' within the Hilbert space denoted by $\{\bar{E}_b\}$:

$$P\left(\bar{E}_a \to \{\bar{E}_b\}\right) = \int\left|\mathcal{M}\left(\bar{E}_a \to \vec{E}_b; {}^{b\neq a}_{t_0\to t}\right)\right|^2\rho\left(\bar{E}_b\right)\mathrm{d}\bar{E}_b. \tag{5.0.51}$$

The $\rho(\bar{E}_b)$ is the density of quantum states at energy $\bar{E}_b$, assuming there is a quasi-continuum of states. In the long time limit, we may invoke the identity (see, for e.g., eq. 5.7.31)

$$\lim_{t\to\infty}\frac{\sin^2(\Delta E\cdot t)}{\Delta E^2\cdot t} = \pi\delta\left(\Delta E\right). \tag{5.0.52}$$

Hence, the total number of late time transitions is

$$P\left(\bar{E}_a \to \{\bar{E}_b\}; t\to\infty\right) = \lim_{t\to\infty}\int|V_{ba}|^2t\frac{\sin\left((\bar{E}_b-\bar{E}_a)t/2\right)^2}{((\bar{E}_b-\bar{E}_a)/2)^2\cdot t}\rho\left(\bar{E}_b\right)\mathrm{d}\bar{E}_b \tag{5.0.53}$$

$$= \int|V_{ba}|^2t(2\pi)\delta\left(\bar{E}_b-\bar{E}_a\right)\rho\left(\bar{E}_b\right)\mathrm{d}\bar{E}_b \tag{5.0.54}$$

$$\equiv 2\pi\langle\langle|V_{ba}|^2\rangle\rangle\rho\left(\bar{E}_b\approx\bar{E}_a\right)\cdot t. \tag{5.0.55}$$

The $\langle\langle|V_{ba}|^2\rangle\rangle$ denotes the average of $|V_{ba}|^2$ over the states $\{\bar{E}_b\}$ that lie very close to $\bar{E}_a$. The rate of transition is simply its time derivative.

$$\frac{\mathrm{d}}{\mathrm{d}t}P\left(\bar{E}_a \to \{\bar{E}_b\approx\bar{E}_a\}; t\to\infty\right) = 2\pi\langle\langle|V_{ba}|^2\rangle\rangle\rho\left(\bar{E}_b\approx\bar{E}_a\right). \tag{5.0.56}$$

Harmonic Perturbation & Fermi's Golden Rule version II Consider a perturbation that is purely harmonic, with positive frequency ($\omega > 0$),

$$H'(t) = -V_0e^{-i\omega t} - V_0^\dagger e^{+i\omega t}. \tag{5.0.57}$$

Here, V_0 is an arbitrary but time-independent perturbation, whose eigenvalues we will assume are much smaller than those of H_0.

For simplicity, let us now consider the case where the system began at some energy eigenstate $\left|\bar{E}_a\right\rangle$ an infinitely long time ago, i.e., $t_0 \to -\infty$; while the observation is made an infinitely long time in the future, i.e., $t \to +\infty$. Eq. (5.0.41) reads

$$\begin{aligned}
&\left|\mathcal{M}\left(\bar{E}_a \to \vec{E}_b; \tfrac{b\neq a}{t_0\to t}\right)\right|^2 \qquad (5.0.58)\\
&\approx \left|\int_{\mathbb{R}} e^{i(\bar{E}_b-\bar{E}_a)s}\, {}_{\mathrm{s}}\left\langle \bar{E}_b \left| V_0 e^{-i\omega\tau} + V_0^\dagger e^{+i\omega\tau}\right| \bar{E}_a\right\rangle_{\mathrm{s}} \mathrm{d}\tau\right|^2\\
&= \left|{}_{\mathrm{s}}\left\langle \bar{E}_b \left| V_0(2\pi)\delta\left(\bar{E}_a-\bar{E}_b+\omega\right) + V_0^\dagger(2\pi)\delta\left(\bar{E}_a-\bar{E}_b-\omega\right)\right| \bar{E}_a\right\rangle_{\mathrm{s}}\right|^2\\
&= \left|(2\pi)\delta\left(\bar{E}_a+\omega-\bar{E}_b\right)\, {}_{\mathrm{s}}\left\langle \bar{E}_b \left| V_0\right| \bar{E}_a\right\rangle_{\mathrm{s}}\right|^2 + \left|(2\pi)\delta\left(\bar{E}_a-\omega-\bar{E}_b\right)\, {}_{\mathrm{s}}\left\langle \bar{E}_b \left| V_0^\dagger\right| \bar{E}_a\right\rangle_{\mathrm{s}}\right|^2.
\end{aligned}$$

In the last line, there are no cross terms, which would otherwise contain $\delta(\bar{E}_a-\bar{E}_b-\omega)\delta(\bar{E}_a-\bar{E}_b+\omega)$, because it is not possible for the arguments to be simultaneously equal to zero; namely

$$\bar{E}_a - \bar{E}_b = \omega = -\omega \qquad (5.0.59)$$

cannot be true unless $\omega = 0$. In fact, the two Dirac δ-functions correspond to

- $\bar{E}_a+\omega = \bar{E}_b$: (Absorption of $\omega-$quanta) Ending up with a higher energy indicates an external quanta of energy ω was absorbed.
- $\bar{E}_a-\omega = \bar{E}_b$: (Emission of $\omega-$quanta) Ending up with a lower energy indicates an external quanta of energy ω was emitted.

Now, there is a mathematical issue with the last equality of eq. (5.0.58). It contains terms like

$$\left((2\pi)\delta\left(\bar{E}_a-\bar{E}_b-\omega\right)\right)^2 = (2\pi)\delta\left(\bar{E}_a-\bar{E}_b-\omega\right)\cdot(2\pi)\delta(0) \qquad \text{and} \qquad (5.0.60)$$

$$\left((2\pi)\delta\left(\bar{E}_a-\bar{E}_b+\omega\right)\right)^2 = (2\pi)\delta\left(\bar{E}_a-\bar{E}_b+\omega\right)\cdot(2\pi)\delta(0)\,. \qquad (5.0.61)$$

The interpretation of the $2\pi\delta(0)$ is as follows

$$\begin{aligned}
\left((2\pi)\delta\left(\bar{E}_a-\bar{E}_b-\omega\right)\right)^2 &= (2\pi)\delta\left(\bar{E}_a-\bar{E}_b-\omega\right)\int_{\mathbb{R}} e^{i(\bar{E}_a-\bar{E}_b-\omega)s}\mathrm{d}s \qquad (5.0.62)\\
&= (2\pi)\delta\left(\bar{E}_a-\bar{E}_b-\omega\right)\lim_{T\to\infty}\int_{-T}^{+T}\mathrm{d}s \qquad (5.0.63)\\
&= (2\pi)\delta\left(\bar{E}_a-\bar{E}_b-\omega\right)\cdot(\infty\text{-time duration}); \qquad (5.0.64)
\end{aligned}$$

Dividing eq. (5.0.58) throughout by $(2\pi)\delta(0)$ then allows us to re-interpret the result as the rate per unit time of transitioning from $\bar{E}_a$ to $\bar{E}_b$. This result is the celebrated *Fermi's Golden Rule*:

$$\frac{\text{Number of } \bar{E}_a\to\bar{E}_b \text{ transitions, with } b\neq a}{\text{Total time}} \equiv \frac{\left|\mathcal{M}\left(\bar{E}_a \to \vec{E}_b; \tfrac{b\neq a}{t_0\to t}\right)\right|^2}{2\pi\delta(0)} \qquad (5.0.65)$$

$$= \underbrace{(2\pi)\delta\left(\bar{E}_a-\bar{E}_b-\omega\right)\left|{}_{\mathrm{s}}\left\langle \bar{E}_b\left|V_0\right|\bar{E}_a\right\rangle_{\mathrm{s}}\right|^2}_{\text{Emission of }\omega-\text{quanta}} + \underbrace{(2\pi)\delta\left(\bar{E}_a-\bar{E}_b+\omega\right)\left|{}_{\mathrm{s}}\left\langle \bar{E}_b\left|V_0^\dagger\right|\bar{E}_a\right\rangle_{\mathrm{s}}\right|^2}_{\text{Absorption of }\omega-\text{quanta}}. \qquad (5.0.66)$$

Rant I consider this derivation to be rather sloppy. Why should one expect first order PT to remain valid over an infinite time period? The original calculation for $|\mathcal{M}|^2$ is a probability – why are we allowed to re-interpret its infinite time limit as a transition rate (i.e., number of transitions per unit time)? Unfortunately, most textbooks do not justify Fermi's Golden Rule very well; my lack of rigor may only be justified – rather unscientifically! – by blaming others: *everyone else does (roughly) the same thing*!

Relation to Weinberg's Discussion [2] Weinberg's §6 stayed within the Schrödinger picture.

$$|\psi(t)\rangle_s = \sum_n \left|\bar{E}_n\right\rangle_{\rm s}\ {}_{\rm s}\left\langle \bar{E}_n\right|\psi(t)\rangle_{\rm s} \tag{5.0.67}$$

$$= \sum_n \left|\bar{E}_n\right\rangle_{\rm s}\ {}_{\rm I}\left\langle \bar{E}_n; t\right|\psi(t)\rangle_{\rm I}\,. \tag{5.0.68}$$

Referring to equations (5.0.24) and (5.0.25), we see that

$$|\psi(t)\rangle_s = \sum_n e^{-i\bar{E}_n(t-t_0)}\left|\bar{E}_n\right\rangle_{\rm s}\ {}_{\rm s}\left\langle \bar{E}_n\left|U_{\rm I}(t,t_0)\right|\psi(t_0)\right\rangle. \tag{5.0.69}$$

Comparison with Weinberg's eq. (6.1.4) reveals the identifications

$$\bar{E}_n \leftrightarrow E_n(\text{Weinberg}) \tag{5.0.70}$$

$$e^{i\bar{E}_a t_0}\left|\bar{E}_a\right\rangle_{\rm s} \leftrightarrow \Psi_n(\text{Weinberg}) \tag{5.0.71}$$

$${}_{\rm s}\left\langle \bar{E}_n\left|U_{\rm I}(t,t_0)\right|\psi(t_0)\right\rangle \leftrightarrow c_n(\text{Weinberg}). \tag{5.0.72}$$

Problem 5.1. Show that this identification is consistent with Weinberg's equation (6.1.5); i.e., show that ${}_{\rm s}\left\langle \bar{E}_n\left|U_{\rm I}(t,t_0)\right|\psi(t_0)\right\rangle$ obeys the same differential equation as Weinberg's $c_n(t)$. Hint: Remember that $U_{\rm I}$ obeys the Schrödinger equation with respect to the perturbation $H'_{\rm I}$, but in the interaction picture. □

Classical Electromagnetic Fields: Plane Waves Let us now consider the electromagnetic Hamiltonian, neglecting the quadratic-in-$\vec{A}$ term:

$$H = \frac{(\vec{p}-e\vec{A})^2}{2m} + e\phi(\vec{x}) \tag{5.0.73}$$

$$\approx \frac{\vec{p}^2 - e(\vec{p}\cdot\vec{A}+\vec{A}\cdot\vec{p})}{2m} + e\phi(\vec{x}). \tag{5.0.74}$$

For an electromagnetic plane wave,

$$\vec{A} = 2\vec{A}_0\cos\left(\vec{k}\cdot\vec{x}-kt\right), \tag{5.0.75}$$

$$= \vec{A}_0\left(e^{i\vec{k}\cdot\vec{x}-ikt}+e^{-i\vec{k}\cdot\vec{x}+ikt}\right), \tag{5.0.76}$$

$$\vec{A}_0\cdot\vec{k} = 0, \qquad k\equiv|\vec{k}|. \tag{5.0.77}$$

The $\vec{A}_0$ is the polarization vector; whereas $\vec{k}/k$ is the propagation direction and k the angular frequency.

It is possible to show, whenever $\vec{\nabla}\cdot\vec{A}=0$, we have $\vec{p}\cdot\vec{A}=\vec{A}\cdot\vec{p}$. For our case

$$\vec{\nabla}\cdot\vec{A} = -2\vec{A}_0\cdot\vec{\nabla}(\vec{k}\cdot\vec{x})\sin\left(\vec{k}\cdot\vec{x}-kt\right) \tag{5.0.78}$$

$$= -2(\vec{A}_0\cdot\vec{k})\sin\left(\vec{k}\cdot\vec{x}-kt\right)=0. \tag{5.0.79}$$

Therefore, we have

$$H = H_0 + H' \tag{5.0.80}$$

$$H_0 = \frac{\vec{p}^2}{2m} - \frac{Ze^2}{r} \tag{5.0.81}$$

$$H' = -\frac{e}{m}\vec{A}\cdot\vec{p} \tag{5.0.82}$$

$$= -Ve^{-ikt} - V^\dagger e^{+ikt} \tag{5.0.83}$$

$$V \equiv \frac{e}{m}(\vec{A}_0\cdot\vec{p})e^{i\vec{k}\cdot\vec{x}}. \tag{5.0.84}$$

We may compute

$$\left\langle \bar{E}_b \left| V_0 \right| \bar{E}_a \right\rangle = \frac{e}{m}\left\langle \bar{E}_b \left| (\vec{A}_0\cdot\vec{p})e^{i\vec{k}\cdot\vec{X}} \right| \bar{E}_a \right\rangle \tag{5.0.85}$$

$$= \frac{e}{m}\vec{A}_0(\vec{k})\cdot\int \mathrm{d}^3\vec{x}' \left(-i\vec{\nabla}_{\vec{x}}\left\langle\vec{x}\right|\bar{E}_b\right\rangle\Big)^\dagger \left\langle\vec{x}\right|\bar{E}_a\right\rangle e^{i\vec{k}\cdot\vec{x}} \tag{5.0.86}$$

$$= \frac{ie}{m}\vec{A}_0(\vec{k})\cdot\int \mathrm{d}^3\vec{x}' \left(\vec{\nabla}_{\vec{x}}\left\langle\vec{x}\right|\bar{E}_b\right\rangle\Big)^\dagger \left\langle\vec{x}\right|\bar{E}_a\right\rangle e^{i\vec{k}\cdot\vec{x}}. \tag{5.0.87}$$

The absorptive cross section σ is defined as the ratio of the rate of energy absorbed by the atom to the energy flux of the electromagnetic field. Now, the energy flux is $(\vec{E}\times\vec{B})\cdot\widehat{k}$.

$$\vec{E} = -\partial_t\vec{A} = -2k\vec{A}_0\sin\left(\vec{k}\cdot\vec{x}-kt\right) \tag{5.0.88}$$

$$\vec{B} = \vec{\nabla}\times\vec{A} = 2(\vec{A}_0\times\vec{k})\sin\left(\vec{k}\cdot\vec{x}-kt\right) \tag{5.0.89}$$

$$\vec{E}\times\vec{B} = -2k\vec{A}_0\times\left(2\vec{A}_0\times\vec{k}\right)\sin^2\left(\vec{k}\cdot\vec{x}-kt\right) \tag{5.0.90}$$

$$= 4k^2|\vec{A}_0|^2\widehat{k}\sin^2\left(\vec{k}\cdot\vec{x}-kt\right). \tag{5.0.91}$$

Therefore

$$\sigma = \frac{\pi}{k|\vec{A}_0|^2}\frac{e^2}{m^2}\left|\left\langle \bar{E}_a \left| (\vec{A}_0\cdot\vec{p})e^{i\vec{k}\cdot\vec{X}} \right| \bar{E}_b \right\rangle\right|^2 \delta\left(\bar{E}_a-\bar{E}_b+k\right). \tag{5.0.92}$$

Dipole Approximation When the wavelength $\sim 2\pi/k$ of the electromagnetic field is much longer than the size of the atom,

$$k \sim \frac{Ze^2}{a_0/Z} \sim \frac{Ze^2}{L_A}, \tag{5.0.93}$$

where L_A is the size of the atom; then the exponential may be replaced with unity to leading order.

$$\left\langle \bar{E}_a \left| (\vec{A}_0 \cdot \vec{p}) e^{i\vec{k}\cdot\vec{X}} \right| \bar{E}_b \right\rangle \approx \left\langle \bar{E}_a \left| \vec{A}_0 \cdot \vec{p} \right| \bar{E}_b \right\rangle . \tag{5.0.94}$$

As Sakurai [3] explains, we may see that

$$2m[X^i, H_0] = [X^i, P_j]P_j + P_j[X^i, P_j] \tag{5.0.95}$$
$$= 2iP_i. \tag{5.0.96}$$

Therefore

$$\left\langle \bar{E}_a \left| V_0 \right| \bar{E}_b \right\rangle \approx \frac{m}{i} \vec{A}_0 \cdot \left\langle \bar{E}_a \left| [\vec{X}, H_0] \right| \bar{E}_b \right\rangle \tag{5.0.97}$$
$$\approx \frac{m}{i} (\bar{E}_b - \bar{E}_a) \vec{A}_0 \cdot \left\langle \bar{E}_a \left| \vec{X} \right| \bar{E}_b \right\rangle . \tag{5.0.98}$$

$$\sigma = \frac{\pi \cdot e^2}{k|\vec{A}_0|^2} (\bar{E}_b - \bar{E}_a)^2 \left| \vec{A}_0 \cdot \left\langle \bar{E}_a \left| \vec{X} \right| \bar{E}_b \right\rangle \right|^2 \delta \left(\bar{E}_a - \bar{E}_b + k \right) . \tag{5.0.99}$$

Photoelectric effect As a toy model of the photoelectric effect, let us compute the amplitude of the electron at ground state of the H atom to be freed from atom itself. That is,

$$\langle \vec{x} | \bar{E}_a \rangle = \exp\left(-r/a_{\mathrm{B}}\right) / \sqrt{\pi a_{\mathrm{B}}^3} \tag{5.0.100}$$
$$\langle \vec{x} | \bar{E}_b \rangle = \exp\left(i\vec{q} \cdot \vec{x}\right) . \tag{5.0.101}$$

The $\langle \vec{x} | \bar{E}_b \rangle$ is an approximate description of the free state of the H atom, with outgoing momentum $\vec{q}$. In this limit, the kinetic energy dominates over the potential, so

$$\left\langle \vec{x} \left| H \right| \bar{E}_b \right\rangle \approx \frac{\vec{q}^2}{2m_e}. \tag{5.0.102}$$

The amplitude now reads

$$\left\langle \vec{E}_b \left| V_0 \right| \vec{E}_a \right\rangle = \frac{e}{m_e} (\vec{A}_0(\vec{k}) \cdot \vec{q}) \int_{\mathbb{R}^3} \mathrm{d}^3\vec{x} \frac{\exp\left(-r/a_{\mathrm{B}}\right)}{\sqrt{\pi a_{\mathrm{B}}^3}} e^{i(\vec{k}-\vec{q})\cdot\vec{x}}. \tag{5.0.103}$$

Put $\vec{k} - \vec{q} = |\vec{k} - \vec{q}|\hat{z}$.

$$\left\langle \vec{E}_b \left| V_0 \right| \vec{E}_a \right\rangle = \frac{e}{m_e} (\vec{A}_0(\vec{k}) \cdot \vec{q})(2\pi) \int_0^\infty \mathrm{d}r \cdot r \frac{\exp\left(-r/a_{\mathrm{B}}\right)}{\sqrt{\pi a_{\mathrm{B}}^3}} \frac{e^{i|\vec{k}-\vec{q}|r} - e^{-i|\vec{k}-\vec{q}|r}}{i|\vec{k}-\vec{q}|} \tag{5.0.104}$$
$$= \frac{4(2\pi)e}{m_e} (\vec{A}_0(\vec{k}) \cdot \vec{q}) \sqrt{\frac{a_B^3}{\pi}} \frac{1}{(1 + a_B^2(\vec{k}-\vec{q})^2)^2} \tag{5.0.105}$$

Therefore, the total rate of transition is given by

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \int_{\mathbb{R}^3} \frac{\mathrm{d}^3\vec{q}}{(2\pi)^3} (64\pi) \frac{e^2}{m_e^2} (\vec{A}_0(\vec{k}) \cdot \vec{q})^2 \frac{a_B^3}{(1 + a_B^2(\vec{k}-\vec{q})^2)^2} (2\pi) \delta \left(\bar{E}_a - \frac{q^2}{2m_e} + k \right) \tag{5.0.106}$$
$$\bar{E}_a = -13.6 \text{ eV}. \tag{5.0.107}$$

Because we are assuming that $k \gg |\bar{E}_a|$, we have $q^2/(2m_e) \approx k$.

$$\frac{\mathrm{d}N}{\mathrm{d}t\mathrm{d}^2\Omega_{\hat{q}}} \approx \int_0^\infty \frac{\mathrm{d}q q^2}{(2\pi)^3}(64\pi)\frac{e^2}{m_e^2}(\vec{A}_0(\vec{k})\cdot\vec{q})^2\frac{a_B^3}{(1+a_B^2(\vec{k}-\vec{q})^2)^2}(2\pi)\delta\left(\frac{q^2}{2m_e}-k\right) \tag{5.0.108}$$

$$= \int_0^\infty \frac{(\mathrm{d}q^2)\sqrt{q^2}}{2(2\pi)^3}(128\pi)\frac{e^2}{m_e}(\vec{A}_0(\vec{k})\cdot\vec{q})^2\frac{a_B^3}{(1+a_B^2(\vec{k}-\vec{q})^2)^2}(2\pi)\delta\left(q^2-2m_e k\right) \tag{5.0.109}$$

$$= \frac{(2m_e k)^{\frac{3}{2}}}{4\pi}(64)\frac{e^2}{m_e}(\vec{A}_0(\vec{k})\cdot\hat{q})^2\left.\frac{a_B^3}{(1+a_B^2(\vec{k}-\vec{q})^2)^2}\right|_{\vec{q}^2=2m_e k}. \tag{5.0.110}$$

Problem 5.2. Transition Rates of Driven SHO Consider the 3D quantum simple harmonic oscillator (SHO) $\vec{X}$ coupled to an external *classical* harmonic oscillator $\vec{q}$.

$$H = \frac{\vec{p}^2}{2m} + \frac{1}{2}m\omega^2\vec{X}^2 + \epsilon\vec{X}\cdot\vec{q}, \tag{5.0.111}$$

$$\vec{q}(t) = \vec{q}_0\cos(\Omega t); \tag{5.0.112}$$

Compute, at leading order in ϵ, the rate of transition Γ from ground state to the 1st excited state of the SHO. □

6 Poisson Brackets, Commutation Relations, & Momentum as the Generator of Translations

Consider an infinite $D-$dimensional flat space. In the Hilbert space spanned by the eigenkets $\{|\vec{x}\rangle\}$ of the position operator $\vec{X}$, the translation operator is unitary and may be written as

$$\mathcal{T}(\vec{d}) = \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x} \left|\vec{x}+\vec{d}\right\rangle \langle\vec{x}| \tag{6.0.1}$$

$$= \exp\left(-i\vec{d}\cdot\vec{P}\right). \tag{6.0.2}$$

Because $\mathcal{T}$ is unitary, the 'momentum' $\vec{P}$ is Hermitian. Strictly speaking, $\vec{P}$ is of dimensions 1/[Length] – i.e., it is not really momentum. To produce an operator that is in fact of dimension [momentum] = [angular momentum]/[length], we need to multiply a dimensionful quantity κ to $\vec{P}$ such that

$$[\kappa][\vec{P}] = [\text{momentum}]. \tag{6.0.3}$$

Because $[\vec{P}] = 1/[\text{Length}]$, we must have

$$[\kappa] = [\text{angular momentum}]. \tag{6.0.4}$$

In Quantum Mechanics, this constant is nothing but $\hbar$:

$$\hbar\vec{P} \equiv \text{momentum}. \tag{6.0.5}$$

Why we would choose to do something like that, has to do with the analogy between the Poisson brackets of classical mechanics and the commutator of quantum mechanics.

Poisson bracket From §(A), we see that the generator of spatial translation in classical mechanics is the momentum p_i, in that

$$\{f(\vec{q},\vec{p}), p_i\}_{\mathrm{PB}} = \frac{\partial f}{\partial q^i}. \tag{6.0.6}$$

The generator of time translation is the Hamilton H, in that

$$\{f(\vec{q}(t),\vec{p}(t)), H\}_{\mathrm{PB}} = \frac{\mathrm{d}}{\mathrm{d}t} f(\vec{q}(t),\vec{p}(t)). \tag{6.0.7}$$

Quantum Dynamics In the Heisenberg picture, and assuming the Hamiltonian H is time-independent, an operator O_{H} obeys the first order in time ODE:

$$\dot{O}_{\mathrm{H}} = \frac{1}{i\hbar}[O_{\mathrm{H}}, H]. \tag{6.0.8}$$

Linear algebra $\{|\vec{x}\rangle\}$ If we assume that, for an arbitrary ket $|\psi\rangle$,

$$\langle\vec{x}| f\left(\vec{X},\vec{P}\right)|\psi\rangle = f\left(\vec{x},-i\vec{\nabla}\right)\langle\vec{x}|\psi\rangle. \tag{6.0.9}$$

This amounts to assuming a certain operator ordering. For example, this would pan out if all the position operators stand to the left and the momentum to the right; for e.g.,

$$\left\langle \vec{x} \left| \vec{X}^2 \vec{P}^2 \right| \psi \right\rangle = \vec{x}^2 (-i)^2 \partial_i \partial_i \left\langle \vec{x} \right| \psi \rangle \,. \tag{6.0.10}$$

Let us now consider

$$\left\langle \vec{x} \left| \left[f\left(\vec{X}, \vec{P}\right), P_j \right] \right| \psi \right\rangle = f\left(\vec{x}, -i\vec{\nabla}\right) \left\langle \vec{x} \right| P_j \left| \psi \right\rangle - (-) i\vec{\nabla} \left\langle \vec{x} \left| f\left(\vec{X}, \vec{P}\right) \right| \psi \right\rangle \tag{6.0.11}$$

$$= -if\left(\vec{x}, -i\vec{\nabla}\right) \partial_j \left\langle \vec{x} \right| \psi \rangle + i\vec{\nabla} \left(f\left(\vec{X}, \vec{P}\right) \left\langle \vec{x} \right| \psi \rangle \right) \tag{6.0.12}$$

$$= i\left(\vec{\nabla} f\left(\vec{X}, \vec{P}\right)\right) \left\langle \vec{x} \right| \psi \rangle \,. \tag{6.0.13}$$

In other words, since $|\psi\rangle$ was arbitrary,

$$\frac{\partial f\left(\vec{X}, \vec{P}\right)}{\partial X^j} = \frac{1}{i} \left[f\left(\vec{X}, \vec{P}\right), P_j \right] . \tag{6.0.14}$$

Notice there is a $\hbar$ in eq. (6.0.8) (I've deliberately restored it); but none in eq. (6.0.14).

Comparison Identifying eq. (6.0.7) with eq. (6.0.8) (as well as $f \leftrightarrow O_{\rm H}$); and eq. (6.0.6) with eq. (6.0.14) – we now see the following classical-quantum correspondence.

- The Poisson bracket $\{\cdot,\cdot\}_{\rm PB}$ in classical mechanics should be identified with the commutator $(i\hbar)^{-1}[\cdot,\cdot]$ of quantum mechanics.
- The Hamiltonian in classical mechanics should be identified with the Hamiltonian in quantum mechanics.
- The momentum in classical mechanics $\vec{P}$ should be identified with the $-i\hbar\vec{\nabla}$ in quantum mechanics (within the position representation).

7 Non-Relativistic Quantum Mechanics: Schrödinger 's equation & Probability Current, Electromagnetism

Total Energy From the previous section, we see that the momentum operator in QM is to be identified with the generator of translations in the following manner:

$$\langle \vec{x}| \, \vec{P} \, |\psi\rangle = -i\hbar\vec{\nabla} \, \langle \vec{x}| \, \psi\rangle \, . \tag{7.0.1}$$

That, in turn, means that the square of the momentum is the (negative) Laplacian:

$$\langle \vec{x}| \, \vec{P}^2 \, |\psi\rangle = -\hbar^2\vec{\nabla}^2 \, \langle \vec{x}| \, \psi\rangle \, . \tag{7.0.2}$$

Within the Hamiltonian formalism, the classical Hamiltonian H itself is usually kinetic plus potential energy V (i.e., total energy). In the previous section, we have also identified the QM Hamilton with the classical one. Since kinetic energy is $\vec{P}^2/(2m)$, we may therefore identify, in non-relativistic QM:

$$\langle \vec{x}| \, H \, |\psi\rangle = \langle \vec{x}| \left(\frac{\vec{P}^2}{2m} + V(\vec{X}) \right) |\psi\rangle \tag{7.0.3}$$

$$= \left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{x}) \right) \langle \vec{x}| \, \psi\rangle \, . \tag{7.0.4}$$

Schrödinger 's equation (3.0.3) now takes the form:

$$i\partial_t \psi(t,\vec{x}) = \left(-\frac{1}{2m}\vec{\nabla}^2 + V(\vec{x}) \right) \psi(t,\vec{x}), \tag{7.0.5}$$

where $\psi(t,\vec{x}) \equiv \langle \vec{x}| \, \psi(t)\rangle$ and $\hbar \equiv 1$.

Probability Current in NR QM In non-relativistic QM,

$$\rho \equiv |\psi(\vec{x})|^2 \tag{7.0.6}$$

is the probability density of finding the particle at $\vec{x}$. The associated (spatial) probability current is

$$\vec{J} = \frac{i}{2m} \left\{ \psi\vec{\nabla}\psi^* - \psi^*\vec{\nabla}\psi \right\} . \tag{7.0.7}$$

Altogether, they obey the conservation equation

$$\frac{\partial\rho}{\partial t} = -\vec{\nabla} \cdot \vec{J}. \tag{7.0.8}$$

This is perhaps best understood by integrating over some finite spatial volume $\mathfrak{D}$; applying Gauss' theorem on the right hand side,

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{\mathfrak{D}} \rho(t,\vec{x}) \mathrm{d}^D\vec{x} = -\int_{\partial\mathfrak{D}} \vec{J}(t,\vec{x}) \cdot \mathrm{d}^{D-1}\vec{\Sigma}. \tag{7.0.9}$$

(The $\mathrm{d}^{D-1}\vec{\Sigma}$ is the directed area element on the boundary of $\mathfrak{D}$, which I denote as $\partial\mathfrak{D}$.) The interpretation is, the rate of change of probability within $\mathfrak{D}$ per unit time is accounted for by the flux of the probability current through the boundary.

Let us turn to verifying eq. (7.0.8) using Schrödinger 's equation (7.0.5).

$$\dot{\rho} = (i\dot{\psi})^*(i\psi) + (i\psi)^*(i\dot{\psi}) \tag{7.0.10}$$

$$= \left(-(2m)^{-1}\vec{\nabla}^2 + V\right)\psi^* \cdot (i\psi) - i\psi^*\left(-(2m)^{-1}\vec{\nabla}^2 + V\right)\psi \tag{7.0.11}$$

$$= i(2m)^{-1}\left(\psi^*\vec{\nabla}^2\psi - \psi\vec{\nabla}^2\psi^*\right). \tag{7.0.12}$$

On the other hand,

$$\vec{\nabla}\cdot\vec{J} = i(2m)^{-1}\vec{\nabla}\cdot\left(\psi\vec{\nabla}\psi^* - \psi^*\vec{\nabla}\psi\right) \tag{7.0.13}$$

$$= i(2m)^{-1}\left(\psi\vec{\nabla}^2\psi^* - \psi^*\vec{\nabla}^2\psi\right) = -\dot{\rho}. \tag{7.0.14}$$

Electromagnetism We turn now to the problem of including electromagnetism. As shown in appendix (A), the non-relativistic Hamiltonian describing a charged point particle is

$$H = \frac{1}{2m}\left(\vec{p} - e\vec{A}\right)^2 + e\phi. \tag{7.0.15}$$

The Schrödinger equation in the position representation thus reads

$$i\partial_t\psi = \left\{-\frac{1}{2m}\left(\partial_i - ieA^i\right)\left(\partial_i - ieA^i\right) + e\phi + V\right\}\psi. \tag{7.0.16}$$

Probability Current & Electromagnetism With the inclusion of electromagnetism, we need to modify the probability current in order for it to remain conserved. The spatial current is

$$J^i = \frac{i}{2m}\left(\psi(D_i\psi)^* - \psi^* D_i\psi\right). \tag{7.0.17}$$

Let's compute its divergence:

$$\partial_i J^i = \frac{i}{2m}\left(\partial_i\psi(\partial_i + ieA^i)\psi^* - \partial_i\psi^*(\partial_i - ieA^i)\psi\right) + \frac{i}{2m}\left(\psi\partial_i(D_i\psi)^* - \psi^*\partial_i D_i\psi\right) \tag{7.0.18}$$

$$= \frac{i}{2m}\left(\partial_i\psi(ieA^i)\psi^* + \partial_i\psi^*(ieA^i)\psi\right) + \frac{i}{2m}\left(\psi\partial_i(D_i\psi)^* - \psi^*\partial_i D_i\psi\right). \tag{7.0.19}$$

On the other hand, we may re-write eq. (7.0.16) as

$$\dot{\psi} = -i\left\{-\frac{1}{2m}\left(\partial_i - ieA^i\right)\left(\partial_i - ieA^i\right) + e\phi + V\right\}\psi \tag{7.0.20}$$

$$= \frac{1}{2m}(i\partial_i D_i + eA^i(\partial_i - ieA^i))\psi - i(e\phi + V)\psi. \tag{7.0.21}$$

Multiplying both sides by ψ^*,

$$\psi^*\dot{\psi} = \frac{1}{2m}(\psi^* i\partial_i D_i\psi - ie\psi^* A^i i\partial_i\psi) - i\frac{e^2}{2m}\vec{A}^2|\psi|^2 - i(e\phi + V)|\psi|^2. \tag{7.0.22}$$

Adding this to its complex conjugate,

$$\partial_t|\psi|^2 = \psi^*\dot{\psi} + \psi\dot{\psi}^* \tag{7.0.23}$$

$$= \frac{i}{2m}(\psi^*\partial_i D_i\psi - \psi\partial_i(D_i\psi)^* - \psi^*(ieA^i)\partial_i\psi - \psi(ieA^i)\partial_i\psi^*). \tag{7.0.24}$$

We have thus proven that the time derivative of the probability density $|\psi|^2$ is the negative divergence of the current:

$$\partial_t|\psi|^2 = -\partial_i J^i. \tag{7.0.25}$$

U_1 Gauge Invariance Let us observe that, if we define the following covariant derivatives

$$D_t \equiv \partial_t + ie\phi, \tag{7.0.26}$$

$$D_i \equiv \partial_i - ieA^i; \tag{7.0.27}$$

then we may re-write Schrödinger's equation in (7.0.16) into the following form

$$iD_t\psi = \left(-\frac{1}{2m}D_iD_i + V\right)\psi. \tag{7.0.28}$$

We shall see that eq. (7.0.28) will remain unchanged if we perform the following simultaneous replacements:

$$\psi \to \exp(i\theta(t,\vec{x}))\psi, \qquad \phi \to \phi - e^{-1}\partial_t\theta \qquad A^i \to A^i + e^{-1}\partial_i\theta. \tag{7.0.29}$$

Let's compute

$$D_t(e^{i\theta}\cdot) = e^{i\theta}(i\dot{\theta} + \partial_t + ie\phi) \tag{7.0.30}$$

$$= e^{i\theta}(\partial_t + i(e\phi + \theta)). \tag{7.0.31}$$

Likewise,

$$D_i(e^{i\theta}\cdot) = e^{i\theta}(i\partial_i\theta + \partial_i - ieA_i) \tag{7.0.32}$$

$$= e^{i\theta}(\partial_i - ie(A_i - \partial_i\theta)). \tag{7.0.33}$$

These results tell us, if we apply the replacement rules of eq. (7.0.29), eq. (7.0.28) will transform into

$$e^{i\theta}iD_t\psi = e^{i\theta}\left(-\frac{1}{2m}D_iD_i + V\right)\psi. \tag{7.0.34}$$

We witness that, this invariance is primarily due to the following fact:

> Under the *local* (i.e., space-time dependent) U_1 replacement rules of eq. (7.0.29), the derivatives in equations (7.0.26) and (7.0.27) – when acting upon the wavefunction – transform covariantly, namely
>
> $$D_t\psi \to e^{i\theta}D_t\psi, \tag{7.0.35}$$
>
> $$D_i\psi \to e^{i\theta}D_i\psi. \tag{7.0.36}$$

Problem 7.1. Lagrangian Formulation Show that the following Lagrangian density

$$\mathcal{L} \equiv \frac{i}{2}(\psi^* D_t\psi - \psi(D_t\psi)^*) - \frac{1}{2m}(D_i\psi)^*(D_i\psi) - V|\psi|^2 \tag{7.0.37}$$

would yield the Schrödinger's equation in eq. (7.0.28). That is, apply the Euler-Lagrange equations either with respect to ψ^*,

$$\partial_t \frac{\partial\mathcal{L}}{\partial\partial_t\psi^*} + \partial_i \frac{\partial\mathcal{L}}{\partial\partial_i\psi^*} = \frac{\partial\mathcal{L}}{\partial\psi^*}; \tag{7.0.38}$$

or to ψ,

$$\partial_t \frac{\partial\mathcal{L}}{\partial\partial_t\psi} + \partial_i \frac{\partial\mathcal{L}}{\partial\partial_i\psi} = \frac{\partial\mathcal{L}}{\partial\psi}; \tag{7.0.39}$$

and show that eq. (7.0.28) is recovered.

Explain why the Lagrangian in eq. (7.0.37) is in fact invariant under the replacements in eq. (7.0.29).

Suppose we consider *global* U_1 transformations, where the θ in eq. (7.0.29) no longer depends on the space-time position $(t, \vec{x})$. Since $\mathcal{L}$ is invariant, if $\theta \ll 1$ so that $\psi \to e^{i\theta}\psi \approx \psi + i\theta\psi$ and $\psi^* \to \psi^* - i\theta\psi^* + \ldots$, we must have

$$\begin{aligned}
&\mathcal{L} \\
&\to \mathcal{L} + \left(\frac{\partial\mathcal{L}}{\partial\partial_t\psi} i\theta\dot{\psi} + \frac{\partial\mathcal{L}}{\partial\partial_i\psi} i\theta\partial_i\psi + \frac{\partial\mathcal{L}}{\partial\psi} i\theta\psi + \text{c.c.}\right) + \mathcal{O}(\theta^2) \\
&= \mathcal{L} + \left\{ i\theta \left\{ \partial_t\left(\frac{\partial\mathcal{L}}{\partial\partial_t\psi}\psi\right) + \partial_i\left(\frac{\partial\mathcal{L}}{\partial\partial_i\psi}\psi\right) + \psi\left(\frac{\partial\mathcal{L}}{\partial\psi} - \partial_t\frac{\partial\mathcal{L}}{\partial\partial_t\psi} - \partial_i\frac{\partial\mathcal{L}}{\partial\partial_i\psi}\right)\right\} + \text{c.c.}\right\} + \cdots = \mathcal{L}
\end{aligned} \tag{7.0.40}$$

where 'c.c.' denotes the complex conjugate of the preceding terms in the brackets. Explain why, when eq. (7.0.28) holds, we must have

$$\partial_t\mathcal{J}^0 = -\partial_i\mathcal{J}^i, \tag{7.0.41}$$

where

$$\mathcal{J}^0 \equiv i\frac{\partial\mathcal{L}}{\partial\partial_t\psi}\psi + \text{c.c.}, \tag{7.0.42}$$

$$\mathcal{J}^i \equiv i\frac{\partial\mathcal{L}}{\partial\partial_i\psi}\psi + \text{c.c.}. \tag{7.0.43}$$

Compute $(\mathcal{J}^0, \mathcal{J}^i)$ from eq. (7.0.37) and compare them with $|\psi|^2$ and J^i in eq. (7.0.17). □

8 Hydrogen-like Atoms

8.1 Separation of Variable Solution: Energy Eigen-functions & -Energies

The stationary-state Schrödinger equation describing an electron's wavefunction ψ around a Hydrogen-like atom is, in spherical coordinates (r, θ, ϕ),

$$\langle \vec{x} \,|H|\, \psi \rangle = E \, \langle \vec{x} | \, \psi \rangle \,, \tag{8.1.1}$$

$$-\frac{1}{2m_e}\vec{\nabla}^2\psi - \frac{Ze^2}{r}\psi = -\frac{1}{2m_e}\left(\frac{1}{r^2}\partial_r\left(r^2\partial_r\psi\right) + \frac{1}{r^2}\vec{\nabla}_{\mathbb{S}^2}\psi\right) - \frac{Ze^2}{r}\psi = -E\psi. \tag{8.1.2}$$

The first term on the left is the non-relativistic kinetic energy $p^2/(2m_e)$, where m_e is the electron mass. The $-Ze^2/r$ is the electric/Coulomb potential experienced by the electron orbiting around a central nucleus with Z protons and e is the fundamental electric charge; and r the radius of the orbit. Moreover, we are going to be interested in bound states for now; so $-E < 0$.

We first perform a separation of variables,

$$\psi(r, \theta, \phi) = R(r)Y_\ell^m(\theta, \phi). \tag{8.1.3}$$

Using the fact that Y_ℓ^m is the eigenfunction of the Laplacian on the unit sphere, with eigenvalue $-\ell(\ell+1)$,

$$\vec{\nabla}_{\mathbb{S}^2} Y_\ell^m = -\ell(\ell+1)Y_\ell^m, \tag{8.1.4}$$

we have

$$-\frac{R''(r)}{2m_e} - \frac{R'(r)}{m_e r} + \left(E + \frac{\ell(\ell+1)}{2m_e r^2} - \frac{Z\cdot e^2}{r}\right)R(r) = 0. \tag{8.1.5}$$

Next, we re-scale

$$\rho \equiv \sqrt{2m_e E}r, \qquad \xi \equiv \sqrt{\frac{2m_e}{E}}e^2 Z; \tag{8.1.6}$$

to obtain

$$-R''(\rho) - \frac{2}{\rho}R'(\rho) + \left(1 - \frac{\xi}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right)R(\rho) = 0. \tag{8.1.7}$$

Next, we apply the ansatz

$$R(\rho) = \rho^\ell \exp(-\rho)F(\rho) \tag{8.1.8}$$

to convert the above ODE into

$$F''(\rho) + 2\left(\frac{\ell+1}{\rho} - 1\right)F'(\rho) + \frac{\xi - 2\ell - 2}{\rho}F(\rho) = 0. \tag{8.1.9}$$

Let's solve it via a power series

$$F(\rho) = \sum_{s=0}^{+\infty} a_s \rho^s. \tag{8.1.10}$$

One would find that

$$\sum_{s=0}^{+\infty} \big((s-1)s a_s \rho^{s-2} + a_s \rho^{s-1}(\xi - 2\ell - 2) - 2s a_s \rho^{s-1} + 2s a_s \rho^{s-2}(\ell+1)\big) = 0. \tag{8.1.11}$$

The only $s = 0$ term is

$$s = 0 : \qquad a_0(\xi - 2\ell - 2)\rho^{-1}. \tag{8.1.12}$$

By replacing $s \to s+1$ in the ρ^{s-2} terms, we see that, for $s \geq 1$, requiring that each independent power of ρ to vanish implies

$$(2(1+s+\ell) - \xi)a_s = (1+s)(s+2\ell+2)a_{s+1}. \tag{8.1.13}$$

Following Weinberg [2] we make the following asymptotic argument. For large s, notice

$$a_{s+1} = \frac{2(1+s+\ell)-\xi}{(1+s)(s+2\ell+2)} a_s \to \frac{2}{s} a_s. \tag{8.1.14}$$

As Weinberg argues, since a_{s+1} and a_s have the same sign for large s, the infinite series is dominated by these large s terms as $\rho \to \infty$. Therefore we may approximate

$$a_s \approx \frac{2}{s} a_{s-1} \approx \frac{2^2}{s(s-1)} a_{s-2} \approx \frac{2^s}{s!} a_0. \tag{8.1.15}$$

Of course, once s is small enough, a_{s+1}/a_s is no longer $2/s$; Weinberg asserts that one should instead write

$$a_s \approx \frac{2^s}{(s+B)!} C, \tag{8.1.16}$$

for constants B and C.[7] As a result, inserting this asymptotic series into equations (8.1.8) and (8.1.10), and assuming B is integer,

$$R(\rho) = \rho^\ell e^{-\rho} \sum_{s=0}^{\infty} a_s \rho^s \approx C \rho^\ell \frac{e^{-\rho}}{(2\rho)^B} \sum_{s=0}^{\infty} \frac{(2\rho)^{s+B}}{(s+B)!} = C' \rho^{\ell - B} e^{-\rho} e^{2\rho} \propto \rho^{\ell - B} e^{+\rho}; \tag{8.1.17}$$

which blows up exponentially quickly at infinity. Since such a wave function cannot be normalized to unity, we therefore require that the series terminate at some $s = s_\star$. If $a_{n+1} = 0$, the recursion relation in eq. (8.1.13) tells us

$$\xi = \sqrt{\frac{2m_e}{E}} e^2 Z = 2(s_\star + \ell + 1) \equiv 2n, \qquad n \geq \ell + 1. \tag{8.1.18}$$

[7] Weinberg does not appear to explain this step very explicitly.

This in turn means $F(\rho)$ is a $s_\star = n-(\ell+1)$ degree polynomial. They are known as generalized Laguerre polynomials $F(\rho) = L^{2\ell+1}_{n-(\ell+1)}(2\rho)$. The first few polynomials are

$$n=1,\ \ell=0:\ L^{2\ell+1}_{n-(\ell+1)}(2\rho) = 1 \tag{8.1.19}$$
$$n=2,\ \ell=0:\ L^{2\ell+1}_{n-(\ell+1)}(2\rho) = 2-2\rho \tag{8.1.20}$$
$$n=2,\ \ell=1:\ L^{2\ell+1}_{n-(\ell+1)}(2\rho) = 1 \tag{8.1.21}$$
$$n=3,\ \ell=0:\ L^{2\ell+1}_{n-(\ell+1)}(2\rho) = 3-6\rho+2\rho^2 \tag{8.1.22}$$
$$n=3,\ \ell=1:\ L^{2\ell+1}_{n-(\ell+1)}(2\rho) = 4-2\rho \tag{8.1.23}$$
$$n=3,\ \ell=2:\ L^{2\ell+1}_{n-(\ell+1)}(2\rho) = 1 \tag{8.1.24}$$

(See here for more information about orthogonal polynomials; in particular, explicit expressions for the generalized Laguerre and its relation to ${}_1F_1$ can be found here.) To sum, the wave function is

$$\langle \vec{x}|\, n,\ell,m\rangle \equiv \psi_{n,\ell,m}(r,\theta,\phi) \tag{8.1.25}$$
$$= \chi_{n,\ell,m}\left(\frac{r}{n\cdot a_{\rm B}}\right)^{\ell}\exp\left(-\frac{r}{n\cdot a_{\rm B}}\right)L^{2\ell+1}_{n-(\ell+1)}\left(\frac{2r}{n\cdot a_{\rm B}}\right)Y^m_\ell(\theta,\phi); \tag{8.1.26}$$

with $\chi_{n,\ell,m}$ chosen so that the $|\psi|^2$ integrates to unity; the energy levels given by

$$-E_n = -\frac{e^4Z^2}{2n^2}m_e \equiv -\frac{1}{2m_e(n\cdot a_{\rm B})^2} \approx -(13.6\text{ eV})\frac{Z^2}{n^2}, \qquad n=1,2,3,\cdots\geq \ell+1; \tag{8.1.27}$$

and the Bohr radius is defined as

$$a_{\rm B} \equiv (m_e e^2 Z)^{-1} \approx 0.5292\times 10^{-8}Z^{-1}\text{cm}. \tag{8.1.28}$$

For each ℓ, there are $2\ell+1$ m states; so altogether, because $n\geq \ell+1$, there is a

$$\sum_{\ell=0}^{n-1}(2\ell+1) = 2n\frac{n-1}{2}+n = \frac{2n(n-1)+2n}{2} = n^2 \tag{8.1.29}$$

fold degeneracy for each nth energy state. Some nomenclature: $\ell=0,1,2,3$ are denoted respectively as s,p,d,f. The (n,ℓ) pair is often stated as $2p\equiv(2,1)$, $1s\equiv(1,0)$, etc.

Problem 8.1. Compute the normalization constants $\chi_{n,\ell,m}$ in eq. (8.1.26) for $n=1,2$ and $\ell\leq n-1$. □

Problem 8.2. Confluent Hypergeometric Function The radial ODE in eq. (8.1.9) corresponds to the one for the confluent hypergeometric function – see here, for instance. Write down the two linearly independent solutions and describe the relevant properties that leads one to conclude $F(\rho) = L^{2\ell+1}_{n-(\ell+1)}(2\rho)$ for the Hydrogen-like atom. □

8.2 Electric Dipole transitions

The electric dipole transition drives the dominant radiation from an atomic system. The transition rate is [2]

$$\Gamma(\alpha \to \beta) = 4(E_a - E_b)^3 \left| \left\langle \ell, m; \alpha \left| \vec{D} \right| \ell', m'; \beta \right\rangle \right|^2, \tag{8.2.1}$$

where the dipole operator itself is

$$\vec{D} = \sum_n e_n \vec{X}_n. \tag{8.2.2}$$

This dipole approximation holds whenever the emitted photon's wavelength is much larger than the size of the atomic system.

8.3 Hydrogen Energies: SO_4 symmetry and the Runge-Lenz Vector

Rotations in 4D In 4D there are $(4^2-4)/2 = 6$ independent rotation generators. To avoid confusion, we will now use capital letters to denote an index that runs between 1 and 3. The Lie Algebra for SO_4 is defined in terms of the 3D ones

$$J^{\mathrm{I}} = \frac{1}{2}\epsilon^{\mathrm{IJK}} J^{\mathrm{JK}} \qquad \Leftrightarrow \qquad \epsilon^{\mathrm{IJK}} J^{\mathrm{I}} = J^{\mathrm{JK}}. \tag{8.3.1}$$

plus the remaining 3 generators $\{J^{\mathrm{I4}}\}$. We have

$$\left[J^{\mathrm{A}}, J^{\mathrm{B}}\right] = i\epsilon^{\mathrm{ABC}} J^{\mathrm{C}} \tag{8.3.2}$$

$$\left[J^{\mathrm{A4}}, J^{\mathrm{B4}}\right] = i\epsilon^{\mathrm{ABC}} J^{\mathrm{C}} \tag{8.3.3}$$

$$\left[J^{\mathrm{A4}}, J^{\mathrm{B}}\right] = i\epsilon^{\mathrm{ABC}} J^{\mathrm{C4}}. \tag{8.3.4}$$

Furthermore, if we define

$$M^{\mathrm{I}}_{\pm} \equiv \frac{J^{\mathrm{I}} \pm J^{\mathrm{I4}}}{2}. \tag{8.3.5}$$

we may re-write the SO_4 Lie Algebra in terms of 2 independent copies of the SO_3 ones.

$$\left[M^{\mathrm{I}}_{+}, M^{\mathrm{J}}_{-}\right] = 0 \qquad \text{and} \qquad \left[M^{\mathrm{I}}_{\pm}, M^{\mathrm{J}}_{\pm}\right] = i\epsilon^{\mathrm{IJK}} M^{\mathrm{K}}_{\pm}. \tag{8.3.6}$$

Hence, the eigenstates of the rotation generators in 4D space may be labeled by two independent pairs of numbers $(\ell_\pm, m_\pm)$; with $\ell_\pm$ non-negative integer/half-integer,

$$\begin{aligned} \vec{M}^2_{\pm} \left| {\ell_+, m_+ \atop \ell_-, m_-} \right\rangle &= \ell_\pm(\ell_\pm + 1) \left| {\ell_+, m_+ \atop \ell_-, m_-} \right\rangle, \qquad \vec{M}^2_{\pm} \equiv M^{\mathrm{I}}_{\pm} M^{\mathrm{I}}_{\pm} \\ M^3_{\pm} \left| {\ell_+, m_+ \atop \ell_-, m_-} \right\rangle &= m_\pm \left| {\ell_+, m_+ \atop \ell_-, m_-} \right\rangle \end{aligned} \tag{8.3.7}$$

and the usual azimuthal numbers $m_\pm \in \{-\ell_\pm, -\ell_\pm + 1, \ldots, \ell_\pm - 1, \ell_\pm\}$.

Laplace-Runge-Lenz Vector: Classical In 3D, the Laplace-Runge-Lenz vector is the conserved quantity – in addition to energy and angular momentum – within non-relativistic systems with a $1/r$ potential. More specifically, suppose our Hamiltonian is

$$H = \frac{\vec{P}^2}{2m} - \frac{Ze^2}{r}. \tag{8.3.8}$$

Then the equations of motion are

$$m\ddot{\vec{x}} = \dot{\vec{p}} = -\vec{\nabla}\left(-\frac{Ze^2}{r}\right) = -\frac{Ze^2}{r^2}\widehat{r}. \tag{8.3.9}$$

Mass times the Laplce-Runge-Lenz vector itself is defined in terms of the momentum $\vec{p}$ and angular momentum $\vec{L}$ as

$$\vec{A} \equiv \frac{1}{2m}\left(\vec{p}\times\vec{L} - \vec{L}\times\vec{p}\right) - \frac{Ze^2}{r}\vec{x}. \tag{8.3.10}$$

(We have written the $\vec{p}\times\vec{L}$ terms in this symmetrized manner so that it becomes a Hermitian operator upon quantization.) Let us check it is in fact constant; remember $\dot{\vec{L}} = 0$.

$$\dot{\vec{A}} = \frac{1}{2m}\left(\dot{\vec{p}}\times\vec{L} - \vec{L}\times\dot{\vec{p}}\right) + \frac{Ze^2}{r^2}\dot{r}\vec{x} - \frac{Ze^2}{r}\dot{\vec{x}} \tag{8.3.11}$$

$$= -\frac{Ze^2}{r^2}\widehat{r}\times(\vec{x}\times\dot{\vec{x}}) + \frac{Ze^2}{r^2}\dot{r}\vec{x} - \frac{Ze^2}{r}\dot{\vec{x}} \tag{8.3.12}$$

$$= -\frac{Ze^2}{r^2}\left((\widehat{r}\cdot\dot{\vec{x}})\vec{x} - (\widehat{r}\cdot\vec{x})\dot{\vec{x}}\right) + \frac{Ze^2}{r^2}\dot{r}\vec{x} - \frac{Ze^2}{r}\dot{\vec{x}} \tag{8.3.13}$$

We have used $\vec{a}\times(\vec{b}\times\vec{c}) = (\vec{a}\cdot\vec{c})\vec{b} - (\vec{a}\cdot\vec{b})\vec{c}$. Now, $\dot{\vec{x}} = \partial_t(r\vec{r}) = \dot{r}\vec{x} + r\dot{\vec{r}}$. But $\widehat{r}\cdot\dot{\widehat{r}} = (1/2)\partial_t(\widehat{r}\cdot\widehat{r}) = (1/2)\partial_t(1) = 0$.

$$\dot{\vec{A}} = -\frac{Ze^2}{r^2}\dot{r}\vec{x} + \frac{Ze^2}{r}\dot{\vec{x}} + \frac{Ze^2}{r^2}\dot{r}\vec{x} - \frac{Ze^2}{r}\dot{\vec{x}} = 0 \tag{8.3.14}$$

Now that we see $\vec{A}$ is constant, let us understand *where* it is pointing. For that, we only need to evaluate it at a convenient location, since it is constant. Suppose we do so along the orbit where it intersects the semi major axis. Then, if we place the orbit on the xy plane such that the former is moving in a counter-clockwise manner and the semi-major axis is along the $\widehat{x}$ direction,

$$\vec{p}\times\vec{L} = m\dot{\vec{x}}\times m(\vec{x}\times\dot{\vec{x}}) \tag{8.3.15}$$

$$= m|\dot{\vec{x}}|(\pm\widehat{y})\times m(\mp r\widehat{x}\times(\pm)|\dot{\vec{x}}|\widehat{y}) \tag{8.3.16}$$

$$= \pm m|\dot{\vec{x}}|\widehat{y}\times\left(-mr|\dot{\vec{x}}|\widehat{z}\right) = \mp m^2 r|\dot{\vec{x}}|^2\widehat{x}. \tag{8.3.17}$$

(The upper sign is when the orbit intersects the positive $x-$axis; and the lower sign when it intersects the negative $x-$axis.) But the magnitude of the angular momentum $|\vec{L}| = mr|\dot{\vec{x}}| \equiv \ell$ is a constant.

$$\vec{p}\times\vec{L} = \mp\frac{\ell^2}{r}\widehat{x}. \tag{8.3.18}$$

YZ: Incomplete!

Laplace-Runge-Lenz Vector: Quantum We now promote both to Hamiltonian and the Laplace-Runge-Lenz vector to operators. Note that

$$\left\{(\vec{p}\times\vec{L})^i\right\}^\dagger = \epsilon^{ijk}\left(p_j L^k\right)^\dagger \tag{8.3.19}$$

$$= \epsilon^{ijk} L^k p_j = (\vec{L}\times\vec{p})^i. \tag{8.3.20}$$

Likewise

$$\left\{(\vec{L}\times\vec{p})^i\right\}^\dagger = (\vec{p}\times\vec{L})^i. \tag{8.3.21}$$

Hence $\vec{A}$ is Hermitian. Now, because H is rotation-invariant, it commutes with $\vec{J}$.

$$\left[L^i, H\right] = 0. \tag{8.3.22}$$

Problem 8.3. Demonstrate that $\vec{A}$ commutes with the Hamiltonian H.

$$[A^i, H] = 0. \tag{8.3.23}$$

□

Bound State Energies We will now see why equations (8.3.23) and (8.3.22) yields a SO_4 symmetry enjoyed by the bound states ($E < 0$) of hydrogen-like atoms. Define

$$N^i \equiv \sqrt{-\frac{m}{2E}} A^i. \tag{8.3.24}$$

Problem 8.4. Show that

$$L^i N^i = 0 = N^i L^i \qquad \text{and} \qquad \vec{N}^2 = -\frac{H}{E}\left(\vec{L}^2 + 1\right) - \frac{Z^2 e^4 m}{2E}. \tag{8.3.25}$$

From the second equality: if $\vec{N}^2$ may be diagonalized, H will then be diagonalized as well. □

If we further define

$$K^i_\pm \equiv \frac{L^i \pm N^i}{2}, \tag{8.3.26}$$

then a direct calculation will show that these $K^i_\pm$ obey

$$\left[K^a_\pm, K^b_\pm\right] = i\epsilon^{abc} K^c_\pm \qquad \text{and} \qquad \left[K^a_+, K^b_-\right] = 0. \tag{8.3.27}$$

Comparing these equations to eq. (8.3.6) and recalling equations (8.3.23) and (8.3.22), we learn that these $K^i_\pm$ not only generate rotations in a 4D space, they may be used to generate eigenstates of the Hamiltonian.[8]

$$\left[K^i_\pm, H\right] = 0 \tag{8.3.28}$$

[8]It is important to note, these $\vec{K}$s are Hermitian because both J^i and N^i are. The N^i are Hermitian because the energies are negative – remember the square root factor of re-scaling we performed in eq. (8.3.24).

That is, H *is* invariant under 4D 'rotations'.

Symmetry implies degeneracy By employing the spherical tensor components of N^i and the Wigner-Eckart theorem, we may see why the energy eignstates are degenerate with respect to the angular momentum ℓ. (This approach can apparently be found in Shankar's QM text.) In particular, if

$$\vec{L}^2 \left|E;\ell,m\right\rangle = \ell(\ell+1)\left|E;\ell,\ell\right\rangle \tag{8.3.29}$$

$$H\left|E;\ell,m\right\rangle = E\left|E;\ell,\ell\right\rangle; \tag{8.3.30}$$

we know from eq. (8.3.23) that

$$H\left(N_{\ell'}^{m'}\left|E;\ell,m\right\rangle\right) = N_{\ell'}^{m'} H\left|E;\ell,m\right\rangle \tag{8.3.31}$$

$$= E\left(N_{\ell'}^{m'}\left|E;\ell,m\right\rangle\right). \tag{8.3.32}$$

But by the Wigner-Eckart theorem, we know that $N_1^{\pm 1}\left|E;\ell,\ell\right\rangle$ transforms under rotations like the total angular momentum state $|\ell+1,\ell+1;1\ \ell\rangle$.

$$\left\langle E;\ell,m\right| N_1^{\pm 1}\left|E;\ell,\ell\right\rangle = 0 \tag{8.3.33}$$

In other words, we may start from an eigenstate of $\vec{L}^2$ with eigenvalue ℓ and get to the $\ell+1$ eigenstate while still remaining within the same energy subspace.

Energy eigenvalues Now, let us observe that

$$\vec{K}_\pm^2 = \frac{1}{4}\left(\vec{L}^2 + \vec{N}^2 \pm \vec{L}\cdot\vec{N} \pm \vec{N}\cdot\vec{L}\right). \tag{8.3.34}$$

Eq. (8.3.25) now informs us that

$$\vec{K}_+^2 = \vec{K}_-^2 \equiv \vec{K}^2 = \frac{1}{4}\left(\vec{L}^2 + \vec{N}^2\right). \tag{8.3.35}$$

This in turn tells us, for the system at hand, the eigensystem in eq. (8.3.7) is constrained to obey $\ell_+ = \ell_-$. Next, let us also compute

$$\vec{K}_+^2 + \vec{K}_-^2 = 2\vec{K}^2 = \frac{\vec{L}^2 + \vec{N}^2}{2} \tag{8.3.36}$$

$$\vec{N}^2 = 4\vec{K}^2 - \vec{L}^2 \tag{8.3.37}$$

We may now utilize this result in eq. (8.3.25).

$$4\vec{K}^2 - \left(1 - \frac{H}{E}\right)\vec{L}^2 + \frac{H}{E} = -\frac{Z^2 e^4 m}{2E}. \tag{8.3.38}$$

Let us act both sides on an eigenstate of energy E; namely $|E,\ell_K\rangle$. But first: we have – remember equations (8.3.35) and (8.3.7) –

$$H\left|E,\ell_K\right\rangle = E\left|E,\ell_K\right\rangle \tag{8.3.39}$$

$$\vec{K}^2\left|E,\ell_K\right\rangle = \ell_K(\ell_K+1)\left|E,\ell_K\right\rangle; \tag{8.3.40}$$

and therefore we have arrived at

$$-\frac{Z^2e^4m}{2E}\left|E,\ell_K\right\rangle = 4\left(\ell_K(\ell_K+1)+\frac{1}{4}\right)\left|E,\ell_K\right\rangle \tag{8.3.41}$$

$$= (2\ell_K+1)^2\left|E,\ell_K\right\rangle; \tag{8.3.42}$$

$$E = -\frac{Z^2e^4m}{2n^2}, \qquad n\equiv 2\ell_K+1. \tag{8.3.43}$$

Notice the angular momentum operator has canceled out; and the energy levels only depend on the eigenvalues of $\vec{K}^2$. This is what accounts for the high degree of degeneracy in the hydrogen energy levels – it neither depends on the azimuthal angular momentum number m (which may be attributed to rotation symmetry), nor on the orbital angular momentum ℓ itself. Also recall, ℓ_K can take integer and half-integer values; therefore $n = 1, 2, 3, \ldots$.

9 3D Rotation Symmetry in Quantum Systems

We define quantum dynamics to be rotationally symmetric whenever the Hamilton is a scalar operator under rotations:

$$D(\widehat{R})^\dagger H D(\widehat{R}) = H. \tag{9.0.1}$$

Here, $D(\widehat{R})$ is the rotation operator. The equivalent but infinitesimal version is

$$\left[H, J^i\right] = 0; \tag{9.0.2}$$

where $\vec{J}$ is the total rotation generator.

In particular, if H involves two or more distinct sets of vector operators – say, orbital angular momentum $\{L^i\}$ and spin operators $\{S^i\}$ of a single particle – then the total rotation operator must include generators acting on all relevant spaces. For example, if H involves $\vec{L}$ and $\vec{S}$, then the total rotation generator is

$$\vec{J} = \vec{L} + \vec{S}. \tag{9.0.3}$$

The rotation operator itself, parametrized by the rotation angles $\{\theta^a\}$, is

$$D(\widehat{R}(\vec{\theta})) = \exp\left(-i\theta^a J^a\right) = \exp\left(-i\theta^a\left\{L^a+S^a\right\}\right). \tag{9.0.4}$$

If the Hamilton is a scalar operator it must itself be comprised of scalar operators

$$H = H\left(\vec{L}^2, \vec{S}^2, \vec{L}\cdot\vec{S}\right). \tag{9.0.5}$$

For example, we may have the following spherically symmetric Hamiltonian:

$$H = \frac{\vec{P}^2}{2m} + \alpha\vec{L}\cdot\vec{S} + V(|\vec{X}|); \tag{9.0.6}$$

which transforms as

$$D(\widehat{R})^\dagger H D(\widehat{R}) = \frac{\left(\widehat{R}\vec{P}\right)^2}{2m} + \alpha\left(\widehat{R}\vec{L}\right)\cdot\left(\widehat{R}\vec{S}\right) + V(|\widehat{R}\vec{X}|) \tag{9.0.7}$$

$$= \frac{\vec{P}^2}{2m} + \alpha\vec{L}\cdot\vec{S} + V(|\vec{X}|) = H. \tag{9.0.8}$$

If instead H describes N particles, where the ith particle has angular momentum and spin operators $({}_{(i)}\vec{L},\, {}_{(i)}\vec{S})$, then we have

$$D(\widehat{R}(\vec{\theta})) = \exp\left(-i\vec{\theta}\cdot\vec{J}\right); \tag{9.0.9}$$

where the generator now reads

$$\vec{J} = \sum_{i=1}^{N}\left({}_{(i)}\vec{L} + {}_{(i)}\vec{S}\right). \tag{9.0.10}$$

Energy Eigenstates & Addition of Angular Momentum The importance of rotational symmetry is clear from eq. (9.0.2): the Hamiltonian is mutually compatible with $\vec{J}^2$ and J^3.

$$\left[H, \vec{J}^2\right] = 0 = \left[H, J^3\right] \tag{9.0.11}$$

This is the primary reason why the addition of angular momentum is an important issue within quantum mechanics. For instance, suppose the Hamiltonian describes a single particle with angular momentum $\vec{L}$ and spin operator $\vec{S}$, namely H is given by eq. (9.0.5), then the energy eigenstates are usually not simultaneous eigenstates of $\{\vec{L}^2, \vec{S}^2, L^3, S^3\}$ – i.e.,

$$|\ell, m_1\rangle \otimes |s, m_2\rangle \tag{9.0.12}$$

– where

$$\vec{L}^2\,|\ell, m_1\rangle = \ell(\ell+1)\,|\ell, m_1\rangle \tag{9.0.13}$$

$$L^3\,|\ell, m_1\rangle = m_1\,|\ell, m_1\rangle\,. \tag{9.0.14}$$

and

$$\vec{S}^2\,|s, m_2\rangle = s(s+1)\,|s, m_2\rangle \tag{9.0.15}$$

$$S^3\,|s, m_2\rangle = m_2\,|s, m_2\rangle\,. \tag{9.0.16}$$

The reason is, L^3 and S^3 generate, respectively, rotations about the $3-$axis but only in the angular momentum and spin spaces; and not on the entire physical Hilbert space. As such, the Hamiltonian may not remain invariant under such rotations, even if it is a scalar operator. But instead, we may certainly use the eigenstates of $\{\vec{J}^2, J^3, \vec{L}^2, \vec{S}^2\}$,

$$\vec{J}^2\,|j\ m; \ell\ s\rangle = j(j+1)\,|j\ m; \ell\ s\rangle \tag{9.0.17}$$

$$J^3\,|j\ m; \ell\ s\rangle = m\,|j\ m; \ell\ s\rangle \tag{9.0.18}$$

$$\vec{L}^2\,|j\ m; \ell\ s\rangle = \ell(\ell+1)\,|j\ m; \ell\ s\rangle \tag{9.0.19}$$

$$\vec{S}^2\,|j\ m; \ell\ s\rangle = s(s+1)\,|j\ m; \ell\ s\rangle \tag{9.0.20}$$

$$-j \leq m \leq j. \tag{9.0.21}$$

The j lie between $|\ell - s|$ and $\ell + s$.

$$j \in \{|\ell - s|, |\ell - s| + 1, |\ell - s| + 2, \ldots, \ell + s - 2, \ell + s - 1, \ell + s\}\,. \tag{9.0.22}$$

Also observe that, by expanding out the right hand side of $\vec{J}^2 = (\vec{L} + \vec{S})^2$,

$$\vec{L} \cdot \vec{S} = \frac{1}{2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right). \tag{9.0.23}$$

Hence, the Hamiltonian in eq. (9.0.5) obeys

$$\begin{aligned} &H\left(\vec{L}^2, \vec{S}^2, \vec{L} \cdot \vec{S}\right) |j\ m; \ell\ s\rangle \\ &= H\left(\ell(\ell+1), s(s+1), \frac{1}{2}(j(j+1) - \ell(\ell+1) - s(s+1)), \ldots\right) |j\ m; \ell\ s\rangle\,. \end{aligned} \tag{9.0.24}$$

Notation For an electron orbiting around a nucleus, its energy levels are labeled by a positive integer $n > 1$. To describe its state, the notation

$$^n\ell_j \tag{9.0.25}$$

is used; except instead of using $\ell = 0, 1, 2, 3, \cdots \leq n - 1$, we identify

	s	p	d	f	g
ℓ	0	1	2	3	4

Table (9).

For example, when $n = 1$, $\ell = 0$ and $j = 1/2$, we have $^1s_{1/2}$. The $n = 2$ states allow for $\ell = 0, 1$. In turn, when $\ell = 0$, once again $j = 1/2$; which means we have $^2s_{1/2}$. Whereas when $\ell = 1$, $j = 1/2, 3/2$; this translates to $^2p_{1/2}$ and $^2p_{3/2}$.

Splitting of energy levels due to spin-orbit interaction If H only depends on $\vec{L}^2$ and $\vec{S}^2$, then the energy levels of an electron would be degenerate with respect to the total angular momentum j. Hence, the $\vec{J} \cdot \vec{S} = (1/2)(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$ in eq. (9.0.5) actually acts to 'split' these otherwise degenerate energy levels. (For the hydrogen atom, the energies with the same n and ℓ but different j are known as the *fine structure*. The smaller splits due to the same n and j but different ℓ are known as the *Lamb shift*.)

Problem 9.1. Suppose it is possible to simultaneously measure L^3 and S^3 of an electron in the state $^2p_{1/2}$. Explain what are the possible outcomes; and compute their respective probabilities. Hint: Weinberg [2] Table 4.1 contains the relevant Clebsch-Gordan coefficients. Also note: Weinberg's $C_{j'j''}(j\ m; m'm'')$ is equal to our $\langle j'\ m', j''\ m''|\, j\ m; j'j''\rangle$. □

9.1 'Adding' angular momentum

Let J^i be the generator of rotations, i.e., acting on the entire quantum system at hand. Suppose it is composed of two rotation generators acting on different sectors of the quantum system:

$$J^i \equiv J'^i + J''^i. \tag{9.1.1}$$

That is, the $\vec{J}'$ and $\vec{J}''$ have eigenstates

$$\vec{J}'^2 \left|j_1\ m_1, j_2\ m_2\right\rangle = j_1(j_1+1)\left|j_1\ m_1, j_2\ m_2\right\rangle, \tag{9.1.2}$$

$$\vec{J}''^2 \left|j_1\ m_1, j_2\ m_2\right\rangle = j_2(j_2+1)\left|j_1\ m_1, j_2\ m_2\right\rangle; \tag{9.1.3}$$

and

$$J'^3 \left|j_1\ m_1, j_2\ m_2\right\rangle = m_1\left|j_1\ m_1, j_2\ m_2\right\rangle, \tag{9.1.4}$$

$$J''^3 \left|j_1\ m_1, j_2\ m_2\right\rangle = m_2\left|j_1\ m_1, j_2\ m_2\right\rangle. \tag{9.1.5}$$

Suppose we wish to construct from these states the eigenstates of $\vec{J}^2$ and J^3, which in turn obey

$$\vec{J}^2 \left|j\ m; j'\ j''\right\rangle = j(j+1)\left|j\ m; j'\ j''\right\rangle, \tag{9.1.6}$$

$$J^3 \left|j\ m; j'\ j''\right\rangle = m\left|j\ m; j'\ j''\right\rangle. \tag{9.1.7}$$

We may do so once we know how to compute the Clebsch-Gordan coefficients

$$\{\left\langle j_1\ m_1, j_2\ m_2\right|\left.j\ m; j_1\ j_2\right\rangle\}, \tag{9.1.8}$$

because these angular momentum operators are Hermitian and therefore their eigenstates must span the Hilbert space.

$$\left|j\ m; j_1\ j_2\right\rangle = \sum_{\substack{m_1+m_2=m \\ -j_1\le m_1\le +j_1 \\ -j_2\le m_2\le +j_2}} \left|j_1\ m_1, j_2\ m_2\right\rangle \left\langle j_1\ m_1, j_2\ m_2\right|\left.j\ m; j_1\ j_2\right\rangle. \tag{9.1.9}$$

The rules for adding angular momentum (j_1, m_1) and (j_2, m_2) goes as follows.

- The total angular momentum j runs from $|j_1 - j_2|$ to $j_1 + j_2$ in integer steps.

$$j \in \{|j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2\} \tag{9.1.10}$$

- The azimuthal number m must simply be the sum of the individual ones.

$$m = m_1 + m_2 \tag{9.1.11}$$

As a quick check, one may see that $\{|j_1\ m_1, j_2\ m_2\rangle\}$ spans a $(2j_1+1)(2j_2+1)$ dimensional space, since the 'left' sector is $(2j_1+1)$-dimensional and the 'right' is $(2j_2+1)$-dimensional. On the other hand, for a fixed j, the $|j\ m; j_1\ j_2\rangle$ has m running from $-j$ to $+j$ in integer steps; hence according to the rules above, there are altogether (for $j_1 > j_2$, say)

$$\sum_{j=j_1-j_2}^{j_1+j_2} (2j+1) = (2j_1+1)(2j_2+1) \tag{9.1.12}$$

orthogonal states in total. (The same result would hold if $j_2 > j_1$.)

A direct consequence of these angular momentum addition rules is that half-integer spin (i.e., fermionic) systems can only arise from "adding" odd number of fermionic subsystems. Whereas

integer spin (i.e., bosonic) systems may arise from "adding" even number of fermionic subsystems or arbitrary number of bosonic ones.

Example: Atomic States We will have more to say about atomic states of electrons bound to some central nuclei, but because the electron has intrinsic spin$-1/2$, its total angular momentum in such a system is half-integer $j \pm 1/2$ if j denotes its orbital angular momentum. Namely, here

$$\vec{J} = \vec{L} + \vec{S}, \tag{9.1.13}$$

where the orbital angular momentum is the cross product between the position and linear momentum operators, namely $\vec{L} \equiv \vec{X} \times \vec{P}$; and $\vec{S}$ is the intrinsic-spin operator.

Example: Cooper pairs In superconductivity, electrons may pair up (aka Cooper or BCS pairs) and form bosons.

Example: Neutrons and Protons Neutrons are made up of one u and two d quarks, whereas the proton is made of two u and one d quark. Both n and p have spin$-1/2$, consistent with the spin$-1/2$ character of the individual quarks. (Gluons are involved in the binding of the quarks to form the neutron and proton, but they have intrinsic spin-1.) Of course, they are only 2 out of a plethora of QCD bound states that exist in Nature; see PDG for a comprehensive listing.

Example: 'Orbital' angular momentum and spin-half Let us now consider taking the tensor product

$$|\ell, m\rangle \otimes \left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle; \tag{9.1.14}$$

for integer $\ell = 0, 1, 2, \ldots$ and $-\ell \leq m \leq \ell$. This can be viewed as simultaneously describing the orbital and intrinsic spin of a single electron bound to a central nucleus.

$\ell = 0$ For $\ell = 0$, the only possible total j is $1/2$. Hence,

$$\left|j = \frac{1}{2}\ m = \pm\frac{1}{2}; 0\ \frac{1}{2}\right\rangle = |0, 0\rangle \otimes \left|\frac{1}{2}\ \ \pm\frac{1}{2}\right\rangle. \tag{9.1.15}$$

$\ell \geq 1$ For non-zero ℓ, eq. (**??**) says we must have j running from $\ell - 1/2$ to $\ell + 1/2$:

$$j = \ell \pm \frac{1}{2}. \tag{9.1.16}$$

We start from the highest possible m value.

$$\left|j = \ell + \frac{1}{2}\ m = j; \ell\ \frac{1}{2}\right\rangle = |\ell, \ell\rangle \otimes \left|\frac{1}{2}, \frac{1}{2}\right\rangle. \tag{9.1.17}$$

Applying the lowering operator s times, we have on the left hand side

$$(J^-)^s \left|j = \ell + \frac{1}{2}\ m = j; \ell\ \frac{1}{2}\right\rangle = A_s^{\ell+\frac{1}{2}} \left|j = \ell + \frac{1}{2}\ m = j - s\right\rangle, \tag{9.1.18}$$

where the constant $A_s^{\ell+\frac{1}{2}}$ follows from repeated application of eq. (**??**)

$$A_s^{\ell+\frac{1}{2}} = \prod_{i=0}^{s-1} \sqrt{(2\ell+1-i)(i+1)}. \tag{9.1.19}$$

Whereas on the right hand side, $(J^-)^s = (J'^- + J''^-)^s$ may be expanded using the binomial theorem since $[J'^-, J''^-] = 0$. Altogether,

$$A_s^{\ell+\frac{1}{2}} \left| j = \ell + \frac{1}{2}\ m = j - s; \ell\ \frac{1}{2} \right\rangle = \sum_{i=0}^{s} \binom{s}{i} (J'^-)^{s-i} \left|\ell, \ell\right\rangle \otimes (J''^-)^i \left| \frac{1}{2}, \frac{1}{2} \right\rangle. \tag{9.1.20}$$

But $(J''^-)^i \left|\frac{1}{2}\ \frac{1}{2}\right\rangle = 0$ whenever $i \geq 2$. This means there are only two terms in the sum, which can of course be inferred from the fact that – since the azimuthal number for the spin-half sector can only take 2 values ($\pm 1/2$) – for a fixed total azimuthal number m, there can only be two possible solutions for the $\ell-$sector azimuthal number.

$$\begin{aligned} & A_s^{\ell+\frac{1}{2}} \left| j = \ell + \frac{1}{2}\ m = j - s; \ell\ \frac{1}{2} \right\rangle \\ & = (J'^-)^s \left|\ell, \ell\right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \frac{s!}{(s-1)!} \sqrt{\left(\frac{1}{2}+\frac{1}{2}\right)\left(\frac{1}{2}-\frac{1}{2}+1\right)} (J'^-)^{s-1} \left|\ell, \ell\right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \\ & = A_s^\ell \left|\ell, \ell - s\right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + s \cdot A_{s-1}^\ell \left|\ell, \ell - s + 1\right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle. \end{aligned} \tag{9.1.21}$$

Here, the constants are

$$A_s^\ell = \prod_{i=0}^{s-1} \sqrt{(2\ell - i)(i+1)}, \tag{9.1.22}$$

$$A_{s-1}^\ell = \prod_{i=0}^{s-2} \sqrt{(2\ell - i)(i+1)}. \tag{9.1.23}$$

Writing them out more explicitly,

$$\begin{aligned} & \sqrt{2\ell+1}\sqrt{1}\sqrt{2\ell}\sqrt{2}\sqrt{2\ell-1}\sqrt{3}\ldots\sqrt{2\ell-(s-2)}\sqrt{s} \left| j = \ell + \frac{1}{2}\ m = j - s; \ell\ \frac{1}{2} \right\rangle \\ & = \sqrt{2\ell}\sqrt{1}\sqrt{2\ell-1}\sqrt{2}\sqrt{2\ell-2}\sqrt{3}\ldots\sqrt{2\ell-(s-1)}\sqrt{s} \left|\ell, \ell - s\right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle \\ & \quad + (\sqrt{s})^2 \sqrt{2\ell}\sqrt{1}\sqrt{2\ell-1}\sqrt{2}\sqrt{2\ell-2}\sqrt{3}\ldots\sqrt{2\ell-(s-2)}\sqrt{s-1} \left|\ell, \ell - s + 1\right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle. \end{aligned} \tag{9.1.24}$$

The factors $\sqrt{2\ell}\ldots\sqrt{2\ell-(s-2)}$ and $\sqrt{1}\ldots\sqrt{s}$ are common throughout.

$$\begin{aligned} & \sqrt{2\ell+1} \left| j = \ell + \frac{1}{2}\ m = j - s; \ell\ \frac{1}{2} \right\rangle \\ & \qquad = \sqrt{2\ell-(s-1)} \left|\ell, \ell - s\right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{s} \left|\ell, \ell - s + 1\right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \end{aligned}$$

We use the definition $j - s = \ell + (1/2) - s \equiv m$ to re-express s in terms of m.

$$\left| j = \ell + \frac{1}{2} \;\; m; \ell \; \frac{1}{2} \right\rangle \tag{9.1.25}$$
$$= \frac{1}{\sqrt{2}\sqrt{2\ell+1}} \left(\sqrt{2\ell + 2m + 1} \left| \ell, m - \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{2\ell - 2m + 1} \left| \ell, m + \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \right).$$

(Remember $\ell \pm 1/2$ is half-integer, since ℓ is integer; so the azimuthal number $m \pm 1/2$ itself is an integer.) For the states $|j = \ell - (1/2)\; m\rangle$, we will again see that there are only two terms in the superposition over the tensor product states. For a fixed m, $|j = \ell - (1/2)\; m\rangle$ must be perpendicular to $|j = \ell + (1/2)\; m\rangle$. This allows us to write down its solution (up to an arbitrary phase) by inspecting eq. (9.1.25):

$$\left| j = \ell - \frac{1}{2} \;\; m; \ell \; \frac{1}{2} \right\rangle \tag{9.1.26}$$
$$= \frac{e^{i\delta_{\ell-\frac{1}{2}}}}{\sqrt{2}\sqrt{2\ell+1}} \left(\sqrt{2\ell - 2m + 1} \left| \ell, m - \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, \frac{1}{2} \right\rangle - \sqrt{2\ell + 2m + 1} \left| \ell, m + \frac{1}{2} \right\rangle \otimes \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \right).$$

9.2 Isospin symmetry

The idea of rotation symmetry can be carried over to 'internal symmetries,' where nuclei of similar masses/energies are considered to be the 'same'.

Neutrons and protons: Isospin One-Half The proton has a mass of 938.272 MeV and the neutron 939.565 MeV. Even though the former is electrically charged while the latter is not, this new isospin symmetry would apply primarily to systems governed by the strong force. More specifically, we postulate that the strong interactions are approximately invariant under

$$\begin{bmatrix} p \\ n \end{bmatrix} \to U \begin{bmatrix} p \\ n \end{bmatrix}, \tag{9.2.1}$$

where U is a 2×2 unitary matrix. The U is simply the spin-1/2 representation of the rotation group. We have

$$U = \exp\left(-i\theta^a T^a\right), \qquad T^a = \sigma^a/2 \tag{9.2.2}$$
$$\left[T^a, T^b\right] = i\epsilon^{abc} T^c. \tag{9.2.3}$$

We will regard the proton as the 'spin-up' state

$$T^3 |p\rangle = \frac{1}{2} |p\rangle; \tag{9.2.4}$$

and the neutron to be the 'spin-down' state

$$T^3 |n\rangle = -\frac{1}{2} |n\rangle. \tag{9.2.5}$$

Other nuclei Just as the rotation group allow for different spins, we may assign an isospin t to strong interaction states. For a given t and atomic weight A, the total electric charge obeys

$$Q = e\left(\frac{A}{2} + T^3\right). \tag{9.2.6}$$

As a check: the proton yields $(A/2 + T^3)\,|p\rangle = (1/2 + 1/2)\,|p\rangle = +1\,|p\rangle$; while the neutron $(A/2 + T^3)\,|n\rangle = (1/2 - 1/2)\,|n\rangle = 0\,|n\rangle$.

Isospin $t = 1$ The ground states of ^{12}B and ^{12}N, together with an excited state of ^{12}C have the same spin and energies. They form an isospin 1 multiplet.

Pions $(\pi^{\pm}, \pi^0)$ – where $\pi^{\pm}$ are positvely/negatively charged while π^0 is neutral – also form an isospin 1 multiplet. They have nucleon number $A = 0$, so we have

$$T^3\left|\pi^{\pm}\right\rangle = \pm 1\left|\pi^{\pm}\right\rangle, \qquad T^3\left|\pi^0\right\rangle = 0\left|\pi^0\right\rangle. \tag{9.2.7}$$

This is consistent with their electric charges.

Isospin $t = 3/2$ The Δ^{++}, Δ^{+}, Δ^{0}, and Δ^{-} have isospin 3/2, spin 3/2 and masses ≈ 1240 MeV. They decay very rapidly, due to the strong interactions; and because they decay into particles with nucleon number 1, these Δs themselves are assigned $A = 1$. We may also identify

$$T^3\left|\Delta^{++}\right\rangle = \frac{3}{2}\left|\Delta^{++}\right\rangle, \qquad T^3\left|\Delta^{+}\right\rangle = \frac{1}{2}\left|\Delta^{+}\right\rangle, \tag{9.2.8}$$

$$T^3\left|\Delta^{0}\right\rangle = -\frac{1}{2}\left|\Delta^{0}\right\rangle, \qquad T^3\left|\Delta^{-}\right\rangle = -\frac{3}{2}\left|\Delta^{-}\right\rangle. \tag{9.2.9}$$

Again, this identification is consistent with their respective charges $(+2, +1, 0, -1)$. The amplitude of their decay, which must conserve isospin, according to the Wigner-Eckart theorem:

$$\mathcal{M}\left(\Delta^{++} \to \pi^+ + p\right) = \left\langle 1\ 1, \frac{1}{2}\ \frac{1}{2}; \pi^+\ p \middle| \frac{3}{2}\ \frac{3}{2}; 1\ \frac{1}{2}; \Delta^{++} \right\rangle \tag{9.2.10}$$

$$= \left\langle 1\ 1, \frac{1}{2}\ \frac{1}{2} \middle| \frac{3}{2}\ \frac{3}{2}; 1\ \frac{1}{2} \right\rangle \left\langle 1, \frac{1}{2}; \pi^+\ p \middle| \frac{3}{2}; 1\ \frac{1}{2}; \Delta^{++} \right\rangle \tag{9.2.11}$$

$$= \left\langle 1, \frac{1}{2}; \pi^+\ p \middle| \frac{3}{2}; 1\ \frac{1}{2}; \Delta^{++} \right\rangle; \tag{9.2.12}$$

$$\mathcal{M}\left(\Delta^{+} \to \pi^+ + n\right) = \left\langle 1\ 1, \frac{1}{2}\ -\frac{1}{2}; \pi^+\ n \middle| \frac{3}{2}\ \frac{1}{2}; 1\ \frac{1}{2}; \Delta^{+} \right\rangle \tag{9.2.13}$$

$$= \left\langle 1\ 1, \frac{1}{2}\ -\frac{1}{2} \middle| \frac{3}{2}\ \frac{1}{2}; 1\ \frac{1}{2} \right\rangle \left\langle 1, \frac{1}{2}; \pi^+\ n \middle| \frac{3}{2}; 1\ \frac{1}{2}; \Delta^{+} \right\rangle \tag{9.2.14}$$

$$= \frac{1}{\sqrt{3}} \left\langle 1, \frac{1}{2}; \pi^+\ n \middle| \frac{3}{2}; 1\ \frac{1}{2}; \Delta^{+} \right\rangle; \tag{9.2.15}$$

$$\mathcal{M}\left(\Delta^{+} \to \pi^0 + p\right) = \left\langle 1\ 0, \frac{1}{2}\ \frac{1}{2}; \pi^0\ p \middle| \frac{3}{2}\ \frac{1}{2}; 1\ \frac{1}{2}; \Delta^{+} \right\rangle \tag{9.2.16}$$

$$= \left\langle 1\ 0, \frac{1}{2}\ \frac{1}{2} \middle| \frac{3}{2}\ \frac{1}{2}; 1\ \frac{1}{2} \right\rangle \left\langle 1, \frac{1}{2}; \pi^0\ p \middle| \frac{3}{2}; 1\ \frac{1}{2}; \Delta^{+} \right\rangle \tag{9.2.17}$$

$$= \sqrt{\frac{2}{3}} \left\langle 1, \frac{1}{2}; \pi^0\ p \middle| \frac{3}{2}; 1\ \frac{1}{2}; \Delta^{+} \right\rangle. \tag{9.2.18}$$

By the Wigner-Eckart theorem, the

$$\left\langle 1, \frac{1}{2}; \pi^+ \; p \middle| \frac{3}{2}; 1 \; \frac{1}{2}; \Delta^{++} \right\rangle, \qquad \left\langle 1, \frac{1}{2}; \pi^+ \; n \middle| \frac{3}{2}; 1 \; \frac{1}{2}; \Delta^{+} \right\rangle, \qquad \left\langle 1, \frac{1}{2}; \pi^0 \; p \middle| \frac{3}{2}; 1 \; \frac{1}{2}; \Delta^{+} \right\rangle$$

no longer depends on the T^3-eigenvalues of the isospin states. But that means these reduced matrix elements no longer distinguishes between Δ^{++} vs Δ^+; nor between π^+ vs π^0; nor between p and n. Hence, we may denote

$$\left\langle 1, \frac{1}{2}; \pi^+ \; p \middle| \frac{3}{2}; 1 \; \frac{1}{2}; \Delta^{++} \right\rangle = \left\langle 1, \frac{1}{2}; \pi^+ \; n \middle| \frac{3}{2}; 1 \; \frac{1}{2}; \Delta^{+} \right\rangle = \left\langle 1, \frac{1}{2}; \pi^0 \; p \middle| \frac{3}{2}; 1 \; \frac{1}{2}; \Delta^{+} \right\rangle \equiv \mathcal{M}_0$$

and deduce the *ratio* of the decay rates – which is proportional to the square of the amplitudes, namely $\Gamma \propto |\mathcal{M}|^2$ – is given by

$$\frac{\Gamma\left(\Delta^+ \to \pi^+ + n\right)}{\Gamma\left(\Delta^{++} \to \pi^+ + p\right)} = \frac{1}{3}, \tag{9.2.19}$$

$$\frac{\Gamma\left(\Delta^+ \to \pi^0 + p\right)}{\Gamma\left(\Delta^{++} \to \pi^+ + p\right)} = \frac{2}{3}. \tag{9.2.20}$$

Problem 9.2. Verify

$$\Gamma(\Delta^- \to \pi^- + n) = \Gamma(\Delta^{++} \to \pi^+ + p) \tag{9.2.21}$$

$$\Gamma(\Delta^0 \to \pi^- + p) = \Gamma(\Delta^+ \to \pi^+ + n) \tag{9.2.22}$$

$$\Gamma(\Delta^0 \to \pi^0 + n) = \Gamma(\Delta^+ \to \pi^0 + p). \tag{9.2.23}$$

□

10 Symmetry, Degeneracy & Conservation Laws

Symmetry & Degeneracy Since unitary operators may be associated with symmetry transformations, we may now understand the connection between symmetry and degeneracy. In particular, if A is some Hermitian operator, and it forms mutually compatible observables with the Hermitian generators $\{T^a\}$ of some unitary symmetry operator $U(\vec{\xi}) = \exp(-i\vec{\xi} \cdot \vec{T})$, then A must commute with U as well.

$$\left[A, U(\vec{\xi})\right] = 0. \tag{10.0.1}$$

But that implies, if $|\alpha\rangle$ is an eigenket of A with eigenvalue α, namely

$$A\,|\alpha\rangle = \alpha\,|\alpha\rangle\,, \tag{10.0.2}$$

so must $U\,|\alpha\rangle$ be. For, $[A, U] = 0$ leads us to consider

$$[A, U]\,|\alpha\rangle = 0, \tag{10.0.3}$$

$$A(U\,|\alpha\rangle) = UA\,|\alpha\rangle = \alpha(U\,|\alpha\rangle). \tag{10.0.4}$$

If $U|\alpha\rangle$ is not the same ket as $|\alpha\rangle$ (up to an overall phase), then this corresponds to a degeneracy: the physically distinct states $U(\vec{\xi})|\alpha\rangle$ and $|\alpha\rangle$ both correspond to eigenkets of A with the same eigenvalue α.

Symmetry & Conservation Laws Moreover, if the Hermitian operators $\{T^a\}$ generate a symmetry transformation, and if they also commute with the Hamiltonian H, then these observables are conserved – at least whenever H is time independent. Specifically, if

$$[T^a, H] = 0; \tag{10.0.5}$$

then in the Heisenberg picture, if H is time independent, then eq. (4.0.16) says

$$\frac{\mathrm{d}T^a_{\mathrm{H}}}{\mathrm{d}t} = 0. \tag{10.0.6}$$

If $|\alpha\rangle$ is an eigenket of T^a, i.e., $T^a|\alpha\rangle = \alpha|\alpha\rangle$, then it will remain an eigenket under time evolution. If $U(t,t_0) = \exp(-iH(t-t_0))$ is the time evolution operator, we may check

$$T^a\left(U(t,t_0)|\alpha\rangle\right) = U(t,t_0)T^a|\alpha\rangle = \alpha\left(U(t,t_0)|\alpha\rangle\right). \tag{10.0.7}$$

Of course, $|\alpha\rangle$ may belong to a degenerate subspace; so $U|\alpha\rangle$ may not be equal to $|\alpha\rangle$ (up to a phase). Instead, this is linked to the above discussion regarding degeneracy and symmetry, which we may surmise as:

> Under time evolution governed by a time independent Hamiltonian H, the eigenket of an observable T^a would remain within its degenerate subspace if $[T^a, H] = 0$.

11 Spin and Statistics

All electrons in Nature are the same; there is nothing to distinguish one electron from another – unlike macroscopic objects, you cannot for instance put a mark on one electron and put a different one on another, and use these marks to track their trajectories through spacetime. The same can be said about photons. In (perturbative) relativistic quantum field theory (QFT), this is because all indistinguishable particles are vibrations of the same quantum field.

Furthermore, relativistic QFT informs us the N particle quantum state $|\psi_1\psi_2\ldots\psi_N\rangle$ is fully symmetric

$$|\psi_1\ldots\psi_i\ldots\psi_j\ldots\psi_N\rangle = |\psi_1\ldots\psi_j\ldots\psi_i\ldots\psi_N\rangle \qquad (\forall i \neq j) \qquad \text{(Bosons)} \tag{11.0.1}$$

if these N particles are indistinguishable integer spin $s \geq 0$ ones – photons, gluons, $W^{\pm}$ and Z have spin-1 while the Higgs boson has spin 0.

Whereas, the N particle quantum state $|\psi_1\psi_2\ldots\psi_N\rangle$ is fully anti-symmetric

$$|\psi_1\ldots\psi_i\ldots\psi_j\ldots\psi_N\rangle = -|\psi_1\ldots\psi_j\ldots\psi_i\ldots\psi_N\rangle \qquad (\forall i \neq j) \qquad \text{(Fermions)} \tag{11.0.2}$$

if these N particles are indistinguishable half-integer spin ones (i.e., spin $s = n + 1/2$, for $n \geq 0$ integer). Electrons, muons, taus, quarks, neutrinos all have spin$-1/2$.

Weinberg [2] explains, equations (11.0.1) and (11.0.2) holds for spatial dimensions greater than 2. In 2D space, when one swaps two particles in a N-indistinguishable-particle state, the

quantum state picks up a phase factor that is *path dependent* (as opposed to the ± here). Such particles are known as *anyons*.

Bosonic Statistics The fully symmetric condition of eq. (11.0.1) tells us, it is entirely possible to have all the N particles to lie within the same physical state: $|\psi_i\psi_i\dots\psi_i\rangle$ (with N repeated ψ_is).

Fermionic Statistics, Pauli Exclusion The situation is entirely different for half-integer indistinguishable-particles.

> For the N-indistinguishable-particle fermionic state, which obeys eq. (11.0.2), no 2 indistinguishable fermions can occupy the same state.

This is because

$$|\psi_1\dots\psi_i\dots\psi_i\dots\psi_N\rangle = -\,|\psi_1\dots\psi_i\dots\psi_i\dots\psi_N\rangle = 0 \tag{11.0.3}$$

This fundamental fact, usually called the Pauli Exclusion Principle, forms the basis for understanding atomic and nuclear structure and more generally, the stability of matter itself.

Bosonic Wavefunctions In terms of wavefunctions, we may write the N-indistinguishable bosonic state in terms of its one particle ones $\{\psi_n\}$ as the sum of its product, but symmetrized over all the coordinates (spin, momentum/position, etc.) of each of the N particles:

$$\Psi = \frac{1}{\sqrt{N!}} \sum_{\text{permutations } \{i_\ell\}} \psi_1\left(\vec{\xi}_{\Pi(i_1)}\right) \otimes \psi_1\left(\vec{\xi}_{\Pi(i_2)}\right) \otimes \cdots \otimes \psi_1\left(\vec{\xi}_{\Pi(i_N)}\right). \tag{11.0.4}$$

For example, the 2 particle state is

$$\Psi = \frac{1}{\sqrt{2}}\left(\psi_1(\vec{\xi}_1)\otimes\psi_2(\vec{\xi}_2) + \psi_1(\vec{\xi}_2)\otimes\psi_2(\vec{\xi}_1)\right). \tag{11.0.5}$$

Fermionic Wavefunctions In terms of wavefunctions, we may write the N-indistinguishable fermionic state in terms of its one particle ones $\{\psi_n\}$ as the sum of its product, but anti-symmetrized over all the coordinates (spin, momentum/position, etc.) of each of the N particles:

$$\Psi = \frac{1}{\sqrt{N!}} \sum_{\text{permutations } \{i_\ell\}} (\text{sgn of perm.})\psi_1\left(\vec{\xi}_{\Pi(i_1)}\right) \otimes \psi_1\left(\vec{\xi}_{\Pi(i_2)}\right) \otimes \cdots \otimes \psi_1\left(\vec{\xi}_{\Pi(i_N)}\right). \tag{11.0.6}$$

For example, the 2 particle state is

$$\Psi = \frac{1}{\sqrt{2}}\left(\psi_1(\vec{\xi}_1)\otimes\psi_2(\vec{\xi}_2) - \psi_1(\vec{\xi}_2)\otimes\psi_2(\vec{\xi}_1)\right). \tag{11.0.7}$$

This fermionic case may be written as a determinant.

$$\Psi = \frac{1}{\sqrt{N!}}\epsilon^{i_1\dots i_N}\psi_1\left(\vec{\xi}_{i_1}\right) \otimes \psi_1\left(\vec{\xi}_{i_2}\right) \otimes \cdots \otimes \psi_1\left(\vec{\xi}_{i_N}\right); \tag{11.0.8}$$

where the fully anti-symmetric Levi-Civita symbol is defined such that $\epsilon^{12\dots N} \equiv 1$.

11.1 Spin Precession and Rotating Fermions

[9]Consider a spin-1/2 fermion with mass m. Let us consider its interaction with a magnetic field. Its Hamiltonian is given by, in units where $\hbar = 1 = c$,

$$H = -\frac{ge}{2m}\vec{S}\cdot\vec{B}; \tag{11.1.1}$$

where $\vec{S}$ is the spin operator. The g is a particle-dependent constant; for e.g., Sakurai says $g \approx 1.91$ for the neutron.

If $|\pm\rangle$ are the eigenstates of $\vec{S}\cdot\vec{B}$, namely

$$\vec{S}\cdot\vec{B}\,|\pm\rangle = \pm\frac{B}{2}\,|\pm\rangle\,, \tag{11.1.2}$$

we have the stationary states

$$|E_\pm(t)\rangle = \exp(-iHt)\,|\pm\rangle = \exp\left(i\frac{ge}{2m}(\vec{S}\cdot\vec{B})t\right)|\pm\rangle \tag{11.1.3}$$

$$= \exp\left(\pm i\frac{ge}{2m}\frac{B}{2}t\right)|\pm\rangle\,. \tag{11.1.4}$$

The factor of $1/2$ occurring within the eigenvalue of $\vec{S}\cdot\vec{B}$ is due to the fermionic spin-1/2 character of the particle. This same $1/2$ is also responsible for multiplying the wavefunction by $-$ upon a 2π rotation. For instance, if we rotate the spin eigenstates:

$$|\pm\rangle \to D(\widehat{R}(2\pi))\,|\pm\rangle \equiv \exp(-i(2\pi)\widehat{z}\cdot\vec{S})\,|\pm\rangle \tag{11.1.5}$$

$$|\pm\rangle \to \exp(\mp i\pi)\,|\pm\rangle = -\,|\pm\rangle\,. \tag{11.1.6}$$

Suppose we allow a fermion to propagate along two different paths, before recombining them to observe the resulting interference pattern. Along one path we turn on a magnetic field over a finite region; and along the other we do not. If the initial state is prepared as a spin eigenstate (parallel to the $\vec{B}$ field); then, upon recombination, we must have

$$|\pm\rangle \to \exp\left(\pm i\frac{ge}{2m}\frac{B}{2}T\right)e^{i\delta_1}\,|\pm\rangle + e^{i\delta_2}\,|\pm\rangle \tag{11.1.7}$$

$$= e^{i\delta_2}\exp\left(\pm i\frac{ge}{2m}\frac{B}{4}T + \frac{i}{2}(\delta_1-\delta_2)\right)$$
$$\times\left(\exp\left(\pm i\frac{ge}{2m}\frac{B}{4}T + \frac{i}{2}(\delta_1-\delta_2)\right) + \exp\left(\mp i\frac{ge}{2m}\frac{B}{4}T - \frac{i}{2}(\delta_1-\delta_2)\right)\right)|\pm\rangle$$

$$= 2e^{i\delta_2}\exp\left(\pm i\frac{ge}{2m}\frac{B}{4}T\right)\cos\left(\frac{ge}{2m}\frac{B}{4}T + (\delta_1-\delta_2)\right)|\pm\rangle\,. \tag{11.1.8}$$

The T here is the time duration the particle spent inside the magnetic field. The spin$-1/2$ character of the particle can be tested by testing the whether the change in magnetic field ΔB would cause a 2π phase shift in the interference pattern consistent with this result.

$$\Delta\varphi = 2\pi \qquad \Leftrightarrow \qquad \frac{ge}{m}\frac{\Delta B}{4}T = 2\pi. \tag{11.1.9}$$

[9]This section is based on Sakurai.

11.2 Atomic Structure/Periodic Table & Nuclear Structure

Electrons, neutrons and protons are fermions, obeying the Pauli exclusion principle. This plays a key role in the structure of atoms and nuclei.

For generic atomic number $Z \geq 1$, to a decent approximation, the electrons move in a spherically symmetric central potential $V(r)$. Near the nucleus, $V(r) \to -Ze^2/r$; whereas outside the atom, $V(r) \to -e^2/r$ (i.e., screened by the other $Z-1$ electrons). We may label the states as follows

- Principal energy label $n = 1, 2, 3, \cdots \geq 1$.
- Orbital angular momentum $\ell \geq 0$; and $\ell \leq n-1$.
- There are $2(2\ell+1)$ states for a fixed (n, ℓ) pair, where 2 comes from the $\pm 1/2$ spin states of the electron; and $2\ell+1$ coming from the range of L^3 values. (This neglects spin-orbit interactions.)

Unlike the hydrogen atom different ℓ but same n may not yield the same energy. As Weinberg explains, oftentimes larger ℓ yields larger energies (for the same n), because the electron wave function goes as r^ℓ and hence spends less time near the origin. In order of increasing energy, i.e., $E_1 < E_2 < \cdots < E_6 < E_7$,

Shell/E Level	(n, ℓ), Increasing in energy slightly $\to$	No. of states $\sum 2(2\ell+1)$
E_1	$1s = (1,0)$	2
E_2	$2s = (2,0)$, $2p = (2,1)$	2(1)+2(3)=8
E_3	$3s = (3,0)$, $3p = (3,1)$	2(1)+2(3)=8
E_4	$4s = (4,0)$, $3d = (3,2)$, $4p = (4,1)$	2(1)+2(5)+2(3)=18
E_5	$5s = (5,0)$, $4d = (4,2)$, $5p = (5,1)$	2(1)+2(5)+2(3)=18
E_6	$6s = (6,0)$, $4f = (4,3)$, $5d = (5,2)$, $6p = (6,1)$	2(1)+2(7)+2(5)+2(3)=32
E_7	$7s = (7,0)$, $5f = (5,3)$, $7p = (7,1)$, ...	...

Noble gases The chemically inert elements are those with their 'shells' filled. These are helium ($Z = 2$), neon ($Z = 2+8 = 10$), argon ($Z = 2+8+8 = 18$), krypton ($Z = 2+8+8+18 = 36$, xenon ($Z = 2+8+8+18+18 = 54$), and radon ($Z = 2+8+8+18+18+32 = 86$).
Alkaline metals Alkaline metals are those with one extra electron relative to the noble gases. This extra electron may be readily lost/roam easily throughout the metallic solid; thus making alkaline metals chemically reactive. These are lithium ($Z = 2+1 = 3$), sodium ($Z = 2+8+1 = 11$), and potassium ($Z = 2+8+8+1 = 19$).
Alkai Earths Alkali earths have two electrons more than noble gases: beryllium ($Z = 2+2 = 4$), magnesium ($Z = 2+8+2 = 12$), and calcium ($Z = 18+2 = 20$).
Halogens Halogens are elements with one fewer electron than the noble gases: fluorine ($Z = 2+8-1 = 9$), chlorine ($Z = 2+8+8-1 = 17$), bromine ($Z = 2+8+8+18-1 = 35$).
Oxygen & Sulfur Oxygen ($Z = 10-2 = 9$) and sulfur ($Z = 18-2 = 16$) have 2 electrons fewer than noble gases.

Nuclear Structure Inside the nucleus, we don't have a central/core point-like charge. Instead it's a bunch of protons and neutrons. If we do continue to approximate the potential as

a central one, i.e., $V(r)$, and if we assume the origin is a stable point – we may Taylor expand it about the origin as follows:

$$V(r) = V_0 + (\omega^2/2)r^2 + \ldots, \qquad \omega^2 \equiv V''(0). \tag{11.2.1}$$

In other words, the nucleus near the origin should behave like a simple harmonic oscillator. Recall, for a fixed orbital angular momentum ℓ, the 3D SHO oscillator energies go as

$$E_{n,\ell} = \omega\left(2n + \ell + \frac{3}{2}\right), \qquad n = 0, 1, 2, \ldots. \tag{11.2.2}$$

Every adjacent energy level alternates between odd and even parity; so the ground state is even parity, the first excited state is odd, and so on. This means odd ℓ shows up only for odd $2n + \ell$ and even ℓ only for even $2n + \ell$.

Energy (relative to zero-point)	ℓ	No. of states $\sum 2(2\ell + 1)$
0	$s = 0$	2
ω	$p = 1$	2(3)=6
2ω	$s = 0$, $d = 2$	2(1)+2(5)=12
3ω	$p = 1$, $f = 3$	2(3)+2(7)=20

The shell structure for nuclei is

$$Z = 2, 8, 20, 28, 50, 82, 126 \tag{11.2.3}$$

where Z can refer to either protons or neutrons. For example, as Weinberg points out, ^{4}He is 'doubly magic' because it has $Z_p = 2$ protons and $Z_n = 2$ neutrons. This is why it is particularly stable; and is in turn why during the early universe nuclei heavier than ^{4}He were not produced very much. Other doubly magic nuclei are ^{16}O and ^{40}Ca; they are produced in stars more copiously than their neighbors.

Note that our crude simple harmonic oscillator model can only explain the first 3 shells. According to Weinberg, as we move to the higher energy levels, not only does the potential needs to be modified, the spin-orbit $\vec{S} \cdot \vec{L}$ coupling becomes increasingly important. Remember, the total angular momentum $j = \ell \pm 1/2$. For $\ell = 3$, that gives us $j = 6/2 \pm 1/2 = 5/2, 7/2$.

12 Simple Harmonic Oscillator

12.1 One Dimension

The SHO system in 1D is defined by the Hamiltonian

$$H = \frac{1}{2}p^2 + \frac{1}{2}\omega^2 x^2. \tag{12.1.1}$$

Energy Lower Bound To diagonalize this Hamiltonian, we first seek to "complete the square" in the following sense. Consider, for real α,

$$\left(\frac{1}{\sqrt{2}}\left(p - i\alpha x\right)\right)^\dagger \left(\frac{1}{\sqrt{2}}\left(p - i\alpha x\right)\right) = \frac{1}{2}\left(p + i\alpha x\right)\left(p - i\alpha x\right) \tag{12.1.2}$$

$$= \frac{1}{2}\left(p^2 + \alpha^2 x^2\right) + \frac{i\alpha}{2}\left(xp - px\right) \tag{12.1.3}$$

$$= \frac{1}{2}\left(p^2 + \alpha^2 x^2\right) - \frac{\alpha}{2}. \tag{12.1.4}$$

Comparing the last line with eq. (12.1.1), we see that, by choosing $\alpha = \omega$,

$$H = \omega\left(\frac{1}{\sqrt{2\omega}}\left(p - i\omega x\right)\right)^\dagger \left(\frac{1}{\sqrt{2\omega}}\left(p - i\omega x\right)\right) + \frac{\omega}{2} \tag{12.1.5}$$

$$= \omega\left(a^\dagger a + \frac{1}{2}\right); \tag{12.1.6}$$

where we have defined

$$a \equiv \frac{1}{\sqrt{2\omega}}\left(p - i\omega x\right). \tag{12.1.7}$$

We may immediately deduce

$$a^\dagger = \frac{1}{\sqrt{2\omega}}\left(p + i\omega x\right). \tag{12.1.8}$$

We may readily invert this relation to find

$$X = -\frac{i}{\sqrt{2\omega}}\left(a^\dagger - a\right) \qquad \text{and} \qquad P = \sqrt{\frac{\omega}{2}}\left(a^\dagger + a\right). \tag{12.1.9}$$

At this point, we may infer from eq. (12.1.6) that there is a lower bound on the energy levels of the SHO. If $|E_0\rangle$ is the (unit norm) lowest energy eigenstate, and if we denote $|\Psi\rangle \equiv a\,|E_0\rangle$, then

$$\langle E_0\,|H|\,E_0\rangle = E_0\,\langle E_0|\,E_0\rangle = E_0 = \omega\left\langle E_0\left|a^\dagger a + \frac{1}{2}\right|E_0\right\rangle \tag{12.1.10}$$

$$= \omega\left(\left(a\,|E_0\rangle\right)^\dagger\left(a\,|E_0\rangle\right) + \frac{1}{2}\,\langle E_0|\,E_0\rangle\right) \tag{12.1.11}$$

$$= \omega\left(\langle\Psi_0|\,\Psi_0\rangle + \frac{1}{2}\right) \geq \frac{\omega}{2}. \tag{12.1.12}$$

Raising & Lowering (aka "Ladder") Operators The next step is to recognize the roles of a and $a^\dagger$ in equations (12.1.7) and (12.1.8), respectively, "lowering" and "raising" operators.

$$\left[a, a^\dagger\right] = \frac{1}{2\omega}\left[p - i\omega x, p + i\omega x\right] \tag{12.1.13}$$

$$= -\frac{i\omega}{2\omega}\left(\left[x, p\right] - \left[p, x\right]\right) \tag{12.1.14}$$

$$\left[a, a^\dagger\right] = +1. \tag{12.1.15}$$

Whereas

$$[H, a] = \omega \left[a^\dagger a, a\right] = \omega \left(a^\dagger [a, a] + \left[a^\dagger, a\right] a\right) \tag{12.1.16}$$

$$= \omega \left[a^\dagger, a\right] a = -\omega a. \tag{12.1.17}$$

Now $[A, B]^\dagger = -[A^\dagger, B^\dagger]$, hence

$$-\left[H, a^\dagger\right] = -\omega a^\dagger \tag{12.1.18}$$

$$\left[H, a^\dagger\right] = \omega a^\dagger. \tag{12.1.19}$$

Now, if $|E_n\rangle$ is some energy eigenstate, $a^\dagger |E_n\rangle$ is an energy eigenstate with energy $E_n + \omega$ because of eq. (12.1.19):

$$H\left(a^\dagger |E_n\rangle\right) = \left(Ha^\dagger - a^\dagger H + a^\dagger H\right) |E_n\rangle \tag{12.1.20}$$

$$= \left([H, a^\dagger] + E_n a^\dagger\right) |E_n\rangle = \left(\omega a^\dagger + E_n a^\dagger\right) |E_n\rangle \tag{12.1.21}$$

$$= (E_n + \omega) \left(a^\dagger |E_n\rangle\right). \tag{12.1.22}$$

Since $a^\dagger |E_n\rangle \propto |E_n + \omega\rangle$, we must have $(a^\dagger)^\dagger |E_n\rangle = a^\dagger (a^\dagger |E_n\rangle) \propto a^\dagger |E_n + \omega\rangle \propto |E_n + 2\omega\rangle$; i.e., in words: because each application of $a^\dagger$ on an energy eigenstate yields an energy eigenstate with energy $+\omega$ larger than the previous, $\ell \geq 1$ applications must yield

$$(a^\dagger)^\ell |E_n\rangle \propto |E_n + \ell\omega\rangle. \tag{12.1.23}$$

Likewise, if $|E_n\rangle$ is some energy eigenstate, $a |E_n\rangle$ is an energy eigenstate with energy $E_n - \omega$ because of eq. (12.1.17):

$$H(a |E_n\rangle) = (Ha - aH + aH) |E_n\rangle \tag{12.1.24}$$

$$= ([H, a] + E_n a) |E_n\rangle = (-\omega a + E_n a) |E_n\rangle \tag{12.1.25}$$

$$= (E_n - \omega) (a |E_n\rangle). \tag{12.1.26}$$

Iterating this reasoning ℓ times therefore hands us

$$a^\ell |E_n\rangle \propto |E_n - \ell\omega\rangle. \tag{12.1.27}$$

Since there is a lower bound on energy, however, this process cannot continue indefinitely. Suppose $|E_0\rangle$ is the lowest energy eigenstate, because $a |E_0\rangle$ cannot return a lower energy eigenstate, the only consistent answer is zero:

$$a |E_0\rangle = 0. \tag{12.1.28}$$

Energies Recalling eq. (12.1.6), this means the lowest energy eigenstate must obey

$$E_0 |E_0\rangle = \omega \left(a^\dagger a + \frac{1}{2}\right) |E_0\rangle = \frac{\omega}{2} |E_0\rangle; \tag{12.1.29}$$

i.e.,

$$E_0 = \frac{\omega}{2}. \tag{12.1.30}$$

Every application of the raising operator adds ω to the energy level, we must have

$$E_{n\geq 1} = \omega\left(n + \frac{1}{2}\right). \tag{12.1.31}$$

Note that this discussion tells us there cannot be a separate infinite set of energy levels with a lowest energy $E_0 + \varepsilon$, where $\varepsilon < E_1 - E_0$, where E_0 is the lowest of all energies (by assumption). For, the lowering operator acting on it would again be zero, since $E_0 + \varepsilon - \omega < E_0$. But then its energy is uniquely determined by $\omega(a^\dagger a + (1/2))\,|E_0 + \varepsilon\rangle = (\omega/2)\,|E_0 + \varepsilon\rangle$.

Ground State Moreover, eq. (12.1.28) tells us

$$\langle x\,|p - i\omega x|\,E_0\rangle = 0, \tag{12.1.32}$$
$$-i\partial_x\,\langle x|\,E_0\rangle = i\omega x\,\langle x|\,E_0\rangle\,, \tag{12.1.33}$$
$$\partial_x \ln\langle x|\,E_0\rangle = -\omega x, \tag{12.1.34}$$
$$\ln\langle x|\,E_0\rangle = -\frac{\omega}{2}x^2 + \text{constant}, \tag{12.1.35}$$
$$\langle x|\,E_0\rangle = C\exp\left(-\frac{\omega}{2}x^2\right), \tag{12.1.36}$$

for some constant C. This constant may be fixed by demanding the wavefunction to have unit norm. Taking C to be real,

$$\langle E_0|\,E_0\rangle = C^2\int_{-\infty}^{+\infty} e^{-\omega x^2}\mathrm{d}x = 1, \tag{12.1.37}$$
$$C^4\left(\int_{-\infty}^{+\infty} e^{-\omega x^2}\mathrm{d}x\right)^2 = 1, \tag{12.1.38}$$
$$C^4\left(\int_{\mathbb{R}^2} e^{-\omega(x^2+y^2)}\mathrm{d}x\mathrm{d}y\right) = 1, \tag{12.1.39}$$
$$C^4\left(2\pi\int_0^{+\infty} e^{-\omega\rho^2}\rho\mathrm{d}\rho\right) = 1, \tag{12.1.40}$$
$$C^4\left(\frac{2\pi}{-2\omega}\int_0^{+\infty}\frac{\partial}{\partial\rho}e^{-\omega\rho^2}\mathrm{d}\rho\right) = 1, \tag{12.1.41}$$
$$C^4\left(\frac{\pi}{\omega}\right) = 1 \qquad \Rightarrow \qquad C = \left(\frac{\omega}{\pi}\right)^{\frac{1}{4}}. \tag{12.1.42}$$

To sum, up to an overall multiplicative phase, the non-degenerate ground state wavefunction is

$$\langle x|\,E_0\rangle = \left(\frac{\omega}{\pi}\right)^{\frac{1}{4}}\exp\left(-\frac{\omega}{2}x^2\right), \qquad E_0 = \frac{\omega}{2}. \tag{12.1.43}$$

Excited States We already know from equations (12.1.8) and (12.1.23) that

$$\langle x|\,E_n\rangle \propto (-i\partial_x + i\omega x)^\ell\,\langle x|\,E_0\rangle\,. \tag{12.1.44}$$

To normalize this state,

$$\left((a^\dagger)^\ell\,|E_0\rangle\right)^\dagger\left((a^\dagger)^\ell\,|E_0\rangle\right) = \left(a^\dagger(a^\dagger)^{\ell-1}\,|E_0\rangle\right)^\dagger\left((a^\dagger)^\ell\,|E_0\rangle\right) \tag{12.1.45}$$
$$= \left((a^\dagger)^{\ell-1}\,|E_0\rangle\right)^\dagger\left(a(a^\dagger)^\ell\,|E_0\rangle\right). \tag{12.1.46}$$

Let us now prove the following statement:

$$\left[a, (a^\dagger)^\ell\right] = \ell \cdot (a^\dagger)^{\ell-1}. \tag{12.1.47}$$

The $\ell = 1$ case is simply the commutation relation $[a, a^\dagger] = 1$ in eq. (12.1.14). Assuming the $(k > 1)$th case is true, namely $\left[a, (a^\dagger)^k\right] = k \cdot (a^\dagger)^{k-1}$,

$$\left[a, (a^\dagger)^{k+1}\right] = a^\dagger \left[a, (a^\dagger)^k\right] + \left[a, a^\dagger\right] (a^\dagger)^k \tag{12.1.48}$$

$$= a^\dagger \cdot k \cdot (a^\dagger)^{k-1} + (a^\dagger)^k = (k+1) \cdot (a^\dagger)^{k+1}. \tag{12.1.49}$$

Returning to eq. (12.1.46), and keeping in mind eq. (12.1.28), we may now compute

$$a(a^\dagger)^\ell |E_0\rangle = \left(a(a^\dagger)^\ell - (a^\dagger)^\ell a + (a^\dagger)^\ell a\right) |E_0\rangle \tag{12.1.50}$$

$$= \left[a, (a^\dagger)^\ell\right] |E_0\rangle = \ell \cdot (a^\dagger)^{\ell-1} |E_0\rangle\,; \tag{12.1.51}$$

and hence deduce that

$$\left((a^\dagger)^\ell |E_0\rangle\right)^\dagger \left((a^\dagger)^\ell |E_0\rangle\right) = \ell \cdot \left((a^\dagger)^{\ell-1} |E_0\rangle\right)^\dagger \left((a^\dagger)^{\ell-1} |E_0\rangle\right) \tag{12.1.52}$$

$$= \ell(\ell-1) \cdot \left((a^\dagger)^{\ell-2} |E_0\rangle\right)^\dagger \left((a^\dagger)^{\ell-2} |E_0\rangle\right) = \ldots \tag{12.1.53}$$

$$= \ell!\, \langle E_0 | E_0\rangle = \ell!. \tag{12.1.54}$$

To sum: all unit norm excited states may be written as, for $\ell = 1, 2, 3, \ldots,$

$$|E_{\ell\geq 1}\rangle = \frac{(a^\dagger)^\ell}{\sqrt{\ell!}} |E_0\rangle\,, \qquad E_\ell = \omega\left(\ell + \frac{1}{2}\right). \tag{12.1.55}$$

In the position representation,

$$\langle x | E_\ell\rangle = \frac{(\omega/\pi)^{1/4}}{\sqrt{\ell!}} \left(-i\frac{\partial_x - \omega x}{\sqrt{2\omega}}\right)^\ell \exp\left(-\frac{\omega}{2}x^2\right). \tag{12.1.56}$$

Problem 12.1. Parity Explain why $\langle -x | E_\ell\rangle = (-)^\ell \langle x | E_\ell\rangle$. □

Problem 12.2. Differential Equation for Excited States Guided by the result in eq. (12.1.56), we may infer that the excited state eigenfunction must take the following factorized form:

$$\langle x | E_\ell\rangle = Q_\ell(\xi) \langle x | E_0\rangle\,, \tag{12.1.57}$$

where $\xi \equiv \sqrt{\omega}x$. Show that $Q_\ell(\xi)$ obeys

$$Q''_\ell(\xi) - 2\xi Q'_\ell(\xi) + 2\ell Q_\ell(\xi) = 0. \tag{12.1.58}$$

By demanding that the $\xi \to \infty$ limit yields a polynomial; and by comparing its highest power with that obtained with eq. (12.1.56), show that (up to a phase factor)

$$Q_\ell(\xi) = \frac{H_\ell(\xi)}{2^{\ell/2}\sqrt{\ell!}}, \tag{12.1.59}$$

where $H_\ell(\xi)$ is the Hermite polynomial. Hint: The highest power of the Hermite polynomial can be extracted from its power series in eq. 18.5.13 of NIST's DLMF. □

12.2 Schrödinger vs Heisenberg

Schrödinger Picture So far, we have been working within the Schrödinger picture where, if $|\psi(t)\rangle_{\rm s}$ describes a physical system, it obeys the time dependent Schrödinger equation

$$i\partial_t |\psi(t)\rangle = H |\psi(t)\rangle , \tag{12.2.1}$$

whose solution can be written in terms of the evolution operator

$$|\psi(t > t_0)\rangle_{\rm s} = U(t, t_0) |\psi(t_0)\rangle_{\rm s} , \tag{12.2.2}$$

where

$$U(t, t_0) = \exp(-iH(t - t_0)); \tag{12.2.3}$$

Most observables, such as the position and momentum operators, on the other hand, are time-independent. This means their eigenvectors are also time-independent.

Heisenberg Picture On the other hand, in the Heisenberg picture, we switch to a "rotating basis" of sorts, such that the state $|\psi\rangle$ describing the physical system no longer depends on time; but the operators such as position or momentum now do.

We will need to choose a time t_0 where the two pictures coincide. The underlying motivation behind the switching from Schrödinger to Heisenberg pictures is an alternate description of the expectation value of some operator O. Starting in the Schrödinger picture,

$${}_{\rm s}\langle\psi(t)|O_{\rm s}|\psi(t)\rangle_{\rm s} = {}_{\rm s}\langle\psi(t_0)|e^{+iH_{\rm s}(t-t)}O_{\rm s}e^{-iH_{\rm s}(t-t_0)}|\psi(t_0)\rangle_{\rm s} \equiv {}_{\rm H}\langle\psi|O_{\rm H}|\psi\rangle_{\rm H}; \tag{12.2.4}$$

where the Heisenberg picture operator is

$$O_{\rm H}(t) \equiv e^{+iH_{\rm s}(t-t)}O_{\rm s}e^{-iH_{\rm s}(t-t)}. \tag{12.2.5}$$

We may obtain a first order differential equation for such a Heisenberg picture operator. Assuming its Schrödinger picture counterpart does not depend on time,

$$\partial_t O_{\rm H}(t) = i\left[H_{\rm H}, O_{\rm H}(t)\right]. \tag{12.2.6}$$

Note that, for time independent Hamiltonians, their form is picture independent since they commute at all times:

$$H_{\rm H} = e^{iH_{\rm s}(t-t_0)}H_{\rm s}e^{-iH_{\rm s}(t-t_0)} = e^{iH_{\rm s}(t-t_0)}e^{-iH_{\rm s}(t-t_0)}H_{\rm s} = H_{\rm s}. \tag{12.2.7}$$

Also note that, the computation of commutators can be carried out in either picture; for operators A and B and denoting $U(t, t_0) \equiv \exp(-iH_{\rm s}(t - t_0))$,

$$[A_{\rm H}, B_{\rm H}] = U(t,t_0)^\dagger A_{\rm s}U(t,t_0)U(t,t_0)^\dagger B_{\rm s}U(t,t_0) - U(t,t_0)^\dagger B_{\rm s}U(t,t_0)U(t,t_0)^\dagger A_{\rm s}U(t,t_0) \tag{12.2.8}$$

$$= U(t,t_0)^\dagger \left[A_{\rm s}, B_{\rm s}\right] U(t,t_0). \tag{12.2.9}$$

Spectra Since the Heisenberg operators depend on time, the observables now depend on time too. For example, the position operator is

$$X_{\rm H}(t) = e^{+iH_{\rm s}(t-t_0)}X_{\rm s}e^{-iH_{\rm s}(t-t_0)} \tag{12.2.10}$$

and therefore its eigenvectors must "anti-evolve" in time in that

$$|x,t\rangle_{\rm H} = e^{+iH_{\rm s}(t-t_0)}\,|x\rangle_{\rm s}\,. \tag{12.2.11}$$

We may check:

$$\begin{aligned} X_{\rm H}(t)\,|x,t\rangle_{\rm H} &= e^{+iH_{\rm s}(t-t_0)}X_{\rm s}e^{-iH_{\rm s}(t-t_0)}e^{+iH_{\rm s}(t-t_0)}\,|x\rangle_{\rm s} &(12.2.12)\\ &= e^{+iH_{\rm s}(t-t_0)}X_{\rm s}\,|x\rangle_{\rm s} &(12.2.13)\\ &= xe^{+iH_{\rm s}(t-t_0)}\,|x\rangle_{\rm s} = x\,|x,t\rangle_{\rm H}\,. &(12.2.14)\end{aligned}$$

More generally, for any observable $O_{\rm H}$,

$$\begin{aligned} O_{\rm H}(t)\,|\lambda,t\rangle_{\rm H} &= \lambda\,|\lambda,t\rangle_{\rm H}\,, &(12.2.15)\\ |\lambda,t\rangle_{\rm H} &= e^{+iH_{\rm s}(t-t_0)}\,|\lambda\rangle_{\rm s}\,. &(12.2.16)\end{aligned}$$

SHO EoM, Initial Value Problem We may apply these considerations to the SHO situation. Firstly, note that its Hamiltonian in the Heisenberg pictures is

$$\begin{aligned} H_{\rm H} &= e^{iH_{\rm s}(t-t_0)}\left(\frac{1}{2}P_{\rm s}P_{\rm s}+\frac{1}{2}\omega^2X_{\rm s}X_{\rm s}\right)e^{-iH_{\rm s}(t-t_0)} &(12.2.17)\\ &= \frac{1}{2}e^{iH_{\rm s}(t-t_0)}P_{\rm s}e^{-iH_{\rm s}(t-t_0)}e^{iH_{\rm s}(t-t_0)}P_{\rm s}e^{-iH_{\rm s}(t-t_0)} &(12.2.18)\\ &\qquad+\frac{1}{2}\omega^2e^{iH_{\rm s}(t-t_0)}X_{\rm s}e^{-iH_{\rm s}(t-t_0)}e^{iH_{\rm s}(t-t_0)}X_{\rm s}e^{-iH_{\rm s}(t-t_0)} &(12.2.19)\\ &= \frac{1}{2}P_{\rm H}^2+\frac{\omega^2}{2}X_{\rm H}^2. &(12.2.20)\end{aligned}$$

Let us compute the equations-of-motion (EoM) of the position operator in the Heisenberg picture.

$$\begin{aligned} \dot{X}_{\rm H} &= i\,[H_{\rm H},X_{\rm H}] = ie^{iH(t-t_0)}\left[\frac{1}{2}P_{\rm s}^2+\frac{\omega^2}{2}X_{\rm s}^2,X_{\rm s}\right]e^{-iH(t-t_0)} &(12.2.21)\\ &= \frac{i}{2}e^{iH(t-t_0)}\left(P_{\rm s}\,[P_{\rm s},X_{\rm s}]+[P_{\rm s},X_{\rm s}]\,P_{\rm s}\right)e^{-iH(t-t_0)} &(12.2.22)\\ &= ie^{iH(t-t_0)}\left(-iP_{\rm s}\right)e^{-iH(t-t_0)} = P_{\rm H}. &(12.2.23)\end{aligned}$$

$$\begin{aligned} \dot{P}_{\rm H} &= i\,[H_{\rm H},P_{\rm H}] = ie^{iH(t-t_0)}\left[\frac{1}{2}P_{\rm s}^2+\frac{\omega^2}{2}X_{\rm s}^2,P_{\rm s}\right]e^{-iH(t-t_0)} &(12.2.24)\\ &= \frac{i\omega^2}{2}e^{iH(t-t_0)}\left(X_{\rm s}\,[X_{\rm s},P_{\rm s}]+[X_{\rm s},P_{\rm s}]\,X_{\rm s}\right)e^{-iH(t-t_0)} &(12.2.25)\\ &= i\omega^2e^{iH(t-t_0)}\left(iX_{\rm s}\right)e^{-iH(t-t_0)} = -\omega^2X_{\rm H}. &(12.2.26)\end{aligned}$$

This means $\ddot{X}_{\rm H} = \dot{P}_{\rm H} = -\omega^2X_{\rm H}$; we see that the Heisenberg position operator obeys its classical EoM (see also the discussion around eq. (4.0.19)):

$$\ddot{X}_{\rm H}+\omega^2X_{\rm H} = 0. \tag{12.2.27}$$

Like its classical counterpart the solution may be written in terms of sine and cosine:

$$X_{\mathrm{H}}(t) = A\cos\left(\omega(t-t_0)\right) + B\sin\left(\omega(t-t_0)\right); \tag{12.2.28}$$

except A and B are now operators. When $t = t_0$ the sine vanishes and we must recover the Schrödinger picture position operator. This implies $A = X_{\mathrm{s}}$. Whereas, since $\dot{X}_{\mathrm{H}} = P_{\mathrm{H}} = A\omega\sin(\omega(t-t_0)) + B\omega\cos(\omega(t-t))$, we must have when $t = t_0$, $B\cdot\omega = P_{\mathrm{s}}$. Altogether,

$$X_{\mathrm{H}}(t) = X_{\mathrm{s}}\cos\left(\omega(t-t_0)\right) + \frac{P_{\mathrm{s}}}{\omega}\sin\left(\omega(t-t_0)\right). \tag{12.2.29}$$

This leads us to the following insight. Remember that the expectation value of some operator O in the Heisenberg picture with respect to some physical state $|\psi\rangle_{\mathrm{H}} = |\psi(t_0)\rangle_{\mathrm{s}}$ is given by $\langle\psi_0|O_{\mathrm{H}}(t)|\psi_0\rangle$.

$$\begin{aligned}{}_{\mathrm{H}}\langle\psi|X_{\mathrm{H}}(t)|\psi\rangle_{,\mathrm{H}} = \langle\psi(t_0)|X_{\mathrm{s}}|\psi(t_0)\rangle\cos\left(\omega(t-t_0)\right)& \\ + \frac{\sin\left(\omega(t-t_0)\right)}{\omega}\langle\psi(t_0)|P_{\mathrm{s}}|\psi(t_0)\rangle.&\end{aligned} \tag{12.2.30}$$

At the level of expectation values, the Heisenberg picture position operator written in terms of the Schrödinger picture operators is simply the initial value formulation: $\langle X_{\mathrm{H}}(t)\rangle$ is the initial $\langle X\rangle$ and $\langle P\rangle$ (i.e., in the Schrödinger picture) evolved forward in time.

Problem 12.3. Show that eq. (12.2.29) may be expressed as

$$X_{\mathrm{H}}(t) = \frac{1}{\sqrt{2\omega}}\left(\alpha e^{-i\omega(t-t_0)} + \alpha^\dagger e^{i\omega(t-t_0)}\right), \tag{12.2.31}$$

where $\alpha \equiv ia$; with a being the lowering operator of equations (12.1.7), (12.1.8) and (12.1.9).

In quantum field theory, each momentum mode of a given (linear) field operator obeys something analogous to eq. (12.2.27); which in turn implies every momentum mode of the quantum field may be identified with eq. (12.2.31) – where, the raising/lowering operators become creation/destruction operators that create/destroy particles of the particular momentum at hand. □

12.3 Higher Dimensions

The SHO in higher dimensions $D > 1$ is described by

$$H = \frac{1}{2}\vec{P}^2 + \frac{\omega^2}{2}\vec{X}^2. \tag{12.3.1}$$

Spectrum Because this Hamiltonian is the sum of 1D ones, namely

$$H = \frac{1}{2}P_iP_i + \frac{\omega^2}{2}X^iX^i, \tag{12.3.2}$$

we may immediately take the tensor product of 1D SHO to diagonalize it:

$$|n_1,\ldots,n_D\rangle = |E_{n_1}\rangle\otimes\cdots\otimes|E_{n_D}\rangle, \tag{12.3.3}$$

$$H|n_1,\ldots,n_D\rangle = E_{n_1,\ldots,n_D}|n_1,\ldots,n_D\rangle = (E_{n_1}+\ldots E_{n_D})|n_1,\ldots,n_D\rangle \tag{12.3.4}$$

$$= \omega\left(n_1+\cdots+n_D+\frac{D}{2}\right)|n_1,\ldots,n_D\rangle, \tag{12.3.5}$$

where the $\{n_1, \ldots, n_D\}$ are a collection of non-negative integers. This is because, for a fixed i,

$$\left(\frac{1}{2}P_iP_i + \frac{\omega^2}{2}X^iX^i\right)|n_1, \ldots, n_D\rangle \tag{12.3.6}$$

$$= \left(\frac{1}{2}P_iP_i + \frac{\omega^2}{2}X^iX^i\right)|E_{n_1}\rangle \otimes \cdots \otimes |E_{n_D}\rangle \tag{12.3.7}$$

$$= |E_{n_1}\rangle \otimes \cdots \otimes \left(\frac{1}{2}P_iP_i + \frac{\omega^2}{2}X^iX^i\right)|E_{n_i}\rangle \otimes \cdots \otimes |E_{n_D}\rangle = E_{n_i}|n_1, \ldots, n_D\rangle\,. \tag{12.3.8}$$

In the position representation, the corresponding unit norm energy wavefunction is

$$\langle\vec{x}|\, n_1, \ldots, n_D\rangle = \frac{(\omega/\pi)^{D/4}}{\sqrt{n_1!\ldots n_D!}}\prod_{i=1}^{D}\left\{\left(-i\frac{\partial_x - \omega x}{\sqrt{2\omega}}\right)^{n_i}\exp\left(-\frac{\omega}{2}x^ix^i\right)\right\}. \tag{12.3.9}$$

Raising and Lowering Operators There are now D pairs of raising/lowering operators

$$a_i = \frac{1}{\sqrt{2\omega}}\left(P_i - i\omega X^i\right), \tag{12.3.10}$$

$$a_i^\dagger = \frac{1}{\sqrt{2\omega}}\left(P_i + i\omega X^i\right). \tag{12.3.11}$$

They obey

$$\left[a_i, a_j^\dagger\right] = \delta_{ij}, \qquad [a_i, a_j] = 0 = \left[a_i^\dagger, a_j^\dagger\right]; \tag{12.3.12}$$

as well as

$$[H, a_i] = -\omega a_i \qquad \text{and} \qquad \left[H, a_i^\dagger\right] = +\omega a_i^\dagger. \tag{12.3.13}$$

Parity and Rotational Symmetry Under parity $\vec{x} \to -\vec{x}$, we have

$$\langle -\vec{x}|\, n_1, \ldots, n_D\rangle = (-)^{n_1+n_2+\cdots+n_D}\,\langle\vec{x}|\, n_1, \ldots, n_D\rangle\,. \tag{12.3.14}$$

Note too that the Hamiltonian is rotationally symmetric. Hence in 3D, the energy eigenstates must be simultaneous eigenstates of

$$H, \vec{J}^2, J^3, \check{P}. \tag{12.3.15}$$

Three Dimensions We note that, because J_i and $\vec{J}^2$ commutes with the Hamiltonian, we expect that the energy eigenstates $\langle\vec{x}|\, n_1, \ldots, n_D\rangle$ can be built out of the former's eigenstates. In 3D, this means we should be able to write

$$\langle\vec{x}|\, n_1, n_2, n_3\rangle = \sum_{\ell,m}\chi_{\ell,m}^{n_1,n_2,n_3}R_{\ell,m}^{n_1,n_2,n_3}(r)Y_\ell^m(\theta,\phi). \tag{12.3.16}$$

Examining eq. (12.3.9), we see that, for a fixed $\{n_1, n_2, n_3\}$, the raising operators acting on the Gaussian $\exp(-(\omega/2)\vec{x}^2)$ produces at most a degree $n_1 + n_2 + n_3$ polynomial. Hence, the

maximum ℓ in the above sum must be $\ell_{\max} = n_1 + n_2 + n_3$. For each ℓ remember m runs over the $2\ell + 1$ values, from $-\ell$ to $+\ell$. Whereas $\ell_{\min} = 0$; for example, $(a^\dagger)^2 \exp(-(\omega/2)x^2)$ would produce a constant term multiplying the gaussian. However, we have to remember eq. (12.3.14); which in turn implies there must only even parity Y_ℓ^m if $N \equiv n_1 + n_2 + n_3$ were even and odd parity Y_ℓ^m if N were odd.

$$\langle \vec{x}| \, n_1, n_2, n_3 \rangle = \sum_{\substack{\ell=0 \\ \ell \text{ even}}}^{N} \sum_{m=-\ell}^{+\ell} \chi_{\ell,m}^{n_1,n_2,n_3} R_{\ell,m}^{n_1,n_2,n_3}(r) Y_\ell^m(\theta,\phi), \qquad \text{Even } N \equiv n_1 + n_2 + n_3 \quad (12.3.17)$$

$$= \sum_{\substack{\ell=1 \\ \ell \text{ odd}}}^{N} \sum_{m=-\ell}^{+\ell} \chi_{\ell,m}^{n_1,n_2,n_3} R_{\ell,m}^{n_1,n_2,n_3}(r) Y_\ell^m(\theta,\phi), \qquad \text{Odd } N \equiv n_1 + n_2 + n_3. \quad (12.3.18)$$

For even N this means there is 1 term for $\ell = 0$; $2(2) + 1$ for $\ell = 2$; $2(4) + 1$ for $\ell = 4$; and altogether

$$\sum_{k=0}^{N/2} (4k+1) = 4\frac{N+2}{2}\frac{N}{4} + \frac{N+2}{2} = \frac{(N+1)(N+2)}{2} \quad (12.3.19)$$

terms in the superposition of spherical harmonics to form eq. (12.3.9) of a fixed N.

Rotational and parity invariance tells us, for some fixed $N \equiv n_1 + n_2 + n_3$, the simultaneous eigenstate of energy, parity and rotational operators is

$$\langle \vec{x}| \, N, \ell, m \rangle = R_\ell^N(r) Y_\ell^m(\theta,\phi) \quad (12.3.20)$$

which transforms under parity as

$$\langle -\vec{x}| \, N, \ell, m \rangle = (-)^\ell \, \langle \vec{x}| \, N, \ell, m \rangle \, . \quad (12.3.21)$$

On the other hand, the energy eigenstate N is a polynomial of at most degree N, which transforms as

$$\langle -\vec{x}| \, N, \ell, m \rangle = (-)^N \, \langle \vec{x}| \, N, \ell, m \rangle \, . \quad (12.3.22)$$

Altogether

$$n_1 + n_2 + n_3 \equiv N = \ell + 2s, \quad (12.3.23)$$

where s is an arbitrary integer. Hence, the energy levels are

$$E_{N=\ell+2s} = \omega \left(\ell + 2s + \frac{3}{2} \right) . \quad (12.3.24)$$

For even N, ℓ can therefore run from 0 to N; whereas for odd N, ℓ can run from 1 to N.

Problem 12.4. Prove that, for odd $N \equiv n_1 + n_2 + n_3$, there are also $(N+1)(N+2)/2$ terms in eq. (12.3.18). □

Problem 12.5. $N = 2$ **in 3D** Write down all the wave functions $\langle \vec{x}|\, N = 2, \ell, m\rangle$, where $\ell(\ell+1)$ is the eigenvalue of $\vec{J}^2$ and $-\ell \leq m \leq +\ell$ is that of J^3, for a given energy $\omega(N+3/2)$. □

Problem 12.6. Radial Wavefunction Let the energy eigenfunctions of the 3D SHO with eigenvalue E, namely $\langle r, \theta, \phi|\, E\rangle$, be

$$\langle r, \theta, \phi|\, E\rangle = R(\sqrt{\omega} r) Y_\ell^m(\theta, \phi) \exp\left(-\frac{\omega}{2} r^2\right). \tag{12.3.25}$$

Show that the radial wavefunction R obeys

$$R''(\xi) + \frac{2}{\xi}(1-\xi^2)R'(\xi) - \left(3 - \frac{2E}{\omega} + \frac{\ell(\ell+1)}{\xi^2}\right) R(\xi) = 0; \tag{12.3.26}$$

where $\xi \equiv \sqrt{\omega} r$. Can you show the appropriate solutions are

$$R(\xi) = \chi_{n,\ell} \cdot \xi^\ell \, {}_1F_1\left[-n, \frac{3}{2} + \ell, \xi^2\right]; \tag{12.3.27}$$

where n is a non-negative integer and $\chi_{n,\ell}$ is a normalization constant. Explain why the energy levels are described by

$$E = \omega\left(2n + \ell + \frac{3}{2}\right), \qquad n = 0, 1, 2, \ldots. \tag{12.3.28}$$

Using this energy eigenvalue result, and upon re-scaling $R(\xi) = \xi^\ell \rho(\xi^2)$, show that $\rho(\zeta \equiv \xi^2)$ satisfies the generalized Laguerre polynomial ODE

$$\zeta \rho''(\zeta) + \left(\frac{3}{2} + \ell - \zeta\right) \rho'(\zeta) + n\rho(\zeta) = 0. \tag{12.3.29}$$

Hints: The $\ell = 0$ case is already solved. Focus on $\ell > 0$; and examine the $r \to 0$ and $r \to \infty$ limits. You will find that one of the two linearly independent solutions, as $r \to 0$, is not normalizable. The other solution is not normalizable as $r \to \infty$ unless it becomes a polynomial. For this last step, you might need the fact that the Gamma function becomes singular at 0 and the negative integers. □

13 2-body Problem

Problem 13.1. In 2 body problems, where $\vec{X}_{1,2}$ refers to the positions and $\vec{P}_{1,2}$ to their corresponding momentum operators; show that the definitions

$$\vec{R} \equiv \vec{X}_1 - \vec{X}_2, \tag{13.0.1}$$

$$\vec{X}_{\rm CM} \equiv \frac{m_1 \vec{X}_1 + m_2 \vec{X}_2}{m_1 + m_2} \tag{13.0.2}$$

and

$$\vec{P} \equiv \vec{P}_1 + \vec{P}_2 \tag{13.0.3}$$

$$\vec{\Pi}_{\rm CM} \equiv \mu \left(\frac{\vec{P}_1}{m_1} - \frac{\vec{P}_2}{m_2} \right), \qquad \mu \equiv \frac{m_1 m_2}{m_1 + m_2}; \tag{13.0.4}$$

lead to the position representations

$$\left\langle \vec{R}, \vec{X}_{\rm CM} \middle| \vec{P} \middle| \psi \right\rangle = -i\partial_{\vec{X}_{\rm CM}} \left\langle \vec{R}, \vec{X}_{\rm CM} \middle| \psi \right\rangle, \tag{13.0.5}$$

$$\left\langle \vec{R}, \vec{X}_{\rm CM} \middle| \vec{\Pi} \middle| \psi \right\rangle = -i\partial_{\vec{R}} \left\langle \vec{R}, \vec{X}_{\rm CM} \middle| \psi \right\rangle. \tag{13.0.6}$$

□

14 Rigid Body Dynamics in 3D Space

14.1 Classical

Setup By rigid body motion, I mean here a collection of point particles that are fixed in their positions relative to one another but may rotate as a whole around an arbitrary and possibly time-dependent axis. Or a continuous material object that remains fixed in shape and solid throughout its interior, but may rotate/change its orientation as a function of time. Quantitatively, if $\vec{x}(t)$ refers to a point within this rigid body, we say

$$x^a(t) = R^{ab}(t)\underline{x}^b, \tag{14.1.1}$$

where R^{ab} are components of a time-dependent rotation matrix; and $\underline{x}^b$ are a set of time-independent coordinates that may be associated with that of the particle/location in question but relative to some frame co-rotating with the body itself.[10]

Dynamics In reality, there must be some effective inter-particle potential that holds the body together; but within this rigid body assumption we may ignore it since all positions are fixed relative to the body-frame and whatever potential energy must become a constant in this limit. Hence the dynamics must be entirely attributed to the kinetic energy, which we now seek. Focusing on the point particles case, we let the time-dependent coordinate of the nth particle be denoted as $\vec{x}_{(n)}$, such that

$$x^a_{(n)}(t) = R^{ab}(t)\underline{x}^b_{(n)}. \tag{14.1.2}$$

(Remember, the same rotation matrix R^{ab} applies to all particles $\{\vec{x}_{(n)}\}$ because they form a rigid body.) Hence, if m_n is the mass of the nth particle, its velocity is

$$\dot{x}^a_{(n)}(t) = v^a_{(n)} = \dot{R}^{ab}(t)\underline{x}^b_{(n)}; \tag{14.1.3}$$

[10] More specifically, say at $t = 0$, we may view $x^a(t=0) = R^{ab}(t=0)\underline{x}^b$ as the change-of-coordinates from the co-moving body frame coordinate system $\{\underline{x}^a\}$ to the 'ambient frame' one $\{x^a\}$.

and total kinetic energy

$$K = \frac{1}{2}\sum_n m_n \vec{v}_{(n)}^2 \tag{14.1.4}$$

$$= \frac{1}{2}\sum_n m_n \dot{R}^{ap}(t)\dot{R}^{aq}(t)\underline{x}^p_{(n)}\underline{x}^q_{(n)} = \frac{1}{2}N^{pq}\dot{R}^{ap}\dot{R}^{aq}; \tag{14.1.5}$$

$$N^{ab} \equiv \sum_n m_n \underline{x}^a_{(n)}\underline{x}^b_{(n)}. \tag{14.1.6}$$

We should be able to express this kinetic energy solely in terms of angular momentum variables, since the only motion under consideration is rotational. As a first step, we note that viewed as a matrix, the $\{R^{ab}\}$ obeys

$$R^{\mathrm{T}}R = \mathbb{I}. \tag{14.1.7}$$

Since this is true for all time, differentiating it once yields $\dot{R}^{\mathrm{T}}R + R^{\mathrm{T}}\dot{R} = 0$, which in turn implies

$$\dot{R}^{\mathrm{T}}R = -R^{\mathrm{T}}\dot{R}. \tag{14.1.8}$$

On the other hand, since

$$\dot{R}^{\mathrm{T}}R = \left(R^{\mathrm{T}}\dot{R}\right)^{\mathrm{T}}, \tag{14.1.9}$$

we see that $\dot{R}^{\mathrm{T}}R$ is an anti-symmetric matrix. In the 3D space we are in, this anti-symmetry means we may compute its dual:

$$\Omega^a = \frac{1}{2}\epsilon^{abc}(\dot{R}^{\mathrm{T}})^{bf}R^{fc}; \tag{14.1.10}$$

$$\dot{R}^{fa}R^{fb} = \epsilon^{abc}\Omega^c. \tag{14.1.11}$$

We may multiply both sides with R^{ib},

$$\dot{R}^{ia} = R^{ib}\epsilon^{abc}\Omega^c. \tag{14.1.12}$$

Problem 14.1. Relation to vector calculus In vector calculus, we learn that the velocity $\vec{v}(t) \equiv \dot{\vec{x}}(t)$ of some particle at $\vec{x}(t)$ due to rotation about some axis $\widehat{\omega}$ (where $\widehat{\omega}$ is a unit vector) with angular speed ω is given by

$$\dot{\vec{x}}(t) = \vec{v}(t) = \vec{\omega}(t) \times \vec{x}(t), \qquad \vec{\omega} \equiv \omega\widehat{\omega}. \tag{14.1.13}$$

Remember that $x^a(t) = R^{ab}(t)\underline{x}^b$ and the cross product may be written in terms of the Levi-Civita tensor (in 3D flat space). Show that eq. (14.1.13) implies eq. (14.1.12) provided we identify

$$\vec{\Omega} = -\vec{\omega}. \tag{14.1.14}$$

□

Let us now express the kinetic energy in eq. (14.1.5) in terms of Ω^a. Employing eq. (14.1.12),

$$K = \frac{1}{2} N^{ij} R^{ap} \epsilon^{ipq} \Omega^q R^{am} \epsilon^{jmn} \Omega^n. \tag{14.1.15}$$

Because of the orthogonality of the rotation matrices, $R^{ap} R^{am} = \delta^{pm}$.

$$K = \frac{1}{2} N^{ij} \epsilon^{ipq} \Omega^q \epsilon^{jpn} \Omega^n. \tag{14.1.16}$$

Next we exploit the identity

$$\epsilon^{ipq} \epsilon^{jpn} = \delta^i_j \delta^q_n - \delta^i_n \delta^q_j. \tag{14.1.17}$$

to infer

$$K = \frac{1}{2} \left(N^{ii} \delta^{qn} - N^{nq} \right) \Omega^q \Omega^n \equiv \frac{1}{2} \Omega^q I^{qn} \Omega^n, \tag{14.1.18}$$

$$I^{ab} = \sum_n m_n \left(\underline{x}^c_{(n)} \underline{x}^c_{(n)} \delta^{ab} - \underline{x}^a_{(n)} \underline{x}^b_{(n)} \right). \tag{14.1.19}$$

The I^{ab} here is dubbed the moment-of-inertia tensor.

Problem 14.2. Compute the moment-of-intertia tensor (about the center-of-mass) for a triatomic system which we shall approximate as composed of 1 point mass m_1 at

$$\underline{x}^a_{(1)} = \ell(0, 0, 1); \tag{14.1.20}$$

and 2 equal masses m_2 at

$$\underline{x}^a_{(2\pm)} = \frac{m_1}{m_2} \frac{\ell}{2} \left(\pm \tan(\theta), 0, -1 \right). \tag{14.1.21}$$

Verify that $(0, 0, 0)$ is indeed the center-of-mass; and draw a figure to explain where these atoms are located. □

Orbital angular momentum is

$$J^a(t) = \epsilon^{abc} \sum_n m_n x^b_{(n)}(t) \dot{x}^c_{(n)}(t) \tag{14.1.22}$$

$$= \epsilon^{abc} \sum_n m_n R^{bp}(t) \underline{x}^p_{(n)} \dot{R}^{cq}(t) \underline{x}^q_{(n)} \tag{14.1.23}$$

$$= \epsilon^{abc} \sum_n m_n R^{bp}(t) R^{cm} \epsilon^{qml} \Omega^l \underline{x}^p_{(n)} \underline{x}^q_{(n)}. \tag{14.1.24}$$

From the co-factor expansion definition of the determinant, as well as the property of rotation matrices that $\det R = 1$,

$$\epsilon^{abc} R^{ap} R^{bq} R^{cl} = \epsilon^{pql} \tag{14.1.25}$$

$$\epsilon^{cab} R^{ap} R^{bq} = R^{cl} \epsilon^{pql}. \tag{14.1.26}$$

This in turn tells us

$$J^a(t) = \sum_n m_n R^{ac} \epsilon^{pmc} \epsilon^{qml} \Omega^l \underline{x}^p_{(n)} \underline{x}^q_{(n)}. \tag{14.1.27}$$

Using eq. (14.1.17),

$$J^a(t) = \sum_n m_n (\delta^p_q \delta^c_l - \delta^p_l \delta^c_q) R^{ac} \Omega^l \underline{x}^p_{(n)} \underline{x}^q_{(n)} \tag{14.1.28}$$

$$= R^{ac} \sum_n m_n (\underline{x}^p_{(n)} \underline{x}^p_{(n)} \delta^{cl} - \underline{x}^c_{(n)} \underline{x}^l_{(n)}) \Omega^l \tag{14.1.29}$$

$$= R^{ac} I^{cl} \Omega^l \equiv R^{ac} \mathcal{J}^c. \tag{14.1.30}$$

In matrix notation

$$J = R\mathcal{J} \qquad \Leftrightarrow \qquad R^{\mathrm{T}} J = \mathcal{J}. \tag{14.1.31}$$

KE for invertible moment-of-inertia tensor We now notice that, if the moment-of-inertia tensor has an inverse, then

$$\mathcal{J}^a (I^{-1})^{ab} \mathcal{J}^b = (I\Omega)^{\mathrm{T}} I^{-1} (I\Omega) = \Omega^{\mathrm{T}} I I^{-1} I \Omega \tag{14.1.32}$$

$$= \Omega^a I^{ab} \Omega^b. \tag{14.1.33}$$

Recalling the expression for the kinetic energy in eq. (14.1.18), we see that

$$K = \frac{1}{2} \mathcal{J}^a (I^{-1})^{ab} \mathcal{J}^b. \tag{14.1.34}$$

KE for non-invertible moment-of-inertia tensor Now, in a basis where N^{ab} is diagonal, such that

$$N^{ab} = \mathrm{diag}\left(N^1, N^2, N^3\right); \tag{14.1.35}$$

we have

$$I^{ab} = \mathrm{diag}\left(N^2 + N^3, N^1 + N^3, N^1 + N^2\right). \tag{14.1.36}$$

Problem 14.3. Starting from eq. (14.1.35), verify eq. (14.1.36). □

We see that $\mathrm{Tr} N = \sum_n m_n \vec{x}^2_{(n)} \geq 0$. This in turn says the sum of the eigenvalues of N are always non-negative; in fact, all the eigenvalues are non-negative, i.e., $N^i \geq 0$. This in turn means, if I^{ab} is non-invertible, since 2 out of the 3 N^is appear in every diagonal entry of I^{ab} above, that means at least 2 out of 3 of them must be zero. This leaves only one non-zero component, which we shall simply denote at the 3rd:

$$I^{ab} = \mathrm{diag}\left(N^3, N^3, 0\right), \qquad N^1 = N^2 = 0. \tag{14.1.37}$$

In such a situation, we have

$$K = \frac{1}{2} \Omega^1 I^{11} \Omega^1 + \frac{1}{2} \Omega^2 I^{22} \Omega^2 \tag{14.1.38}$$

$$= \frac{1}{2N^3} \left\{ \left(\mathcal{J}^1\right)^2 + \left(\mathcal{J}^2\right)^2 \right\} = \frac{1}{2N^3} \left\{ \vec{\mathcal{J}}^2 - \left(\mathcal{J}^3\right)^2 \right\}. \tag{14.1.39}$$

14.2 Quantum

To quantize the rigid body dynamics, we shall treat the R^{ab} as a 3×3 matrix of Hermitian operators. We will assume they commute among themselves $[R^{ab}, R^{pq}] = 0$; but not with the time derivatives $[R^{ab}, \dot{R}^{pq}] \neq 0$. Moreover, the $\underline{x}_{(n)}$s – and, hence, the moment-of-inertia tensor – remain as numbers. This scheme will ensure the positions $\vec{x}_{(n)}(t)$ commute among themselves; but not with their momentum.

We will in fact quantize the rigid body dynamics by appealing to the angular momentum algebra:

$$\left[J^a, J^b\right] = i\epsilon^{abc} J^c. \tag{14.2.1}$$

Because position must transform as a 3-vector under rotation, we must also have

$$\left[J^a, x^b_{(n)}\right] = i\epsilon^{abc} x^c_{(n)}, \tag{14.2.2}$$

$$\left[J^a, R^{bd}\right] \underline{x}^d_{(n)} = i\epsilon^{abc} R^{cd} \underline{x}^d_{(n)}. \tag{14.2.3}$$

But since these $\{\underline{x}^d_{(n)}\}$ are arbitrary, we deduce that the rotation operators are actually 3-vectors, for a fixed d:

$$\left[J^a, R^{bd}\right] = i\epsilon^{abc} R^{cd}. \tag{14.2.4}$$

In particular, when $a = b$, they commute with the angular momentum operators because the Levi-Civita is fully anti-symmetric.

$$\left[J^a, R^{ad}\right] = 0 \tag{14.2.5}$$

This means when defining the $\mathcal{J}^i$s as operators (cf. eq. (14.1.31)), namely

$$\mathcal{J}^a = J^b R^{ba}, \tag{14.2.6}$$

there is no operator-ordering ambiguity since the repeated index b means $J^b R^{ba} = R^{ba} J^b$. This allows us to write down the Hamiltonian of the rotator system immediately.

Hamiltonian for invertible moment-of-inertia tensor Because energy is entirely kinetic,

$$H = \frac{1}{2} \mathcal{J}^a (I^{-1})^{ab} \mathcal{J}^b. \tag{14.2.7}$$

Hamiltonian for non-invertible moment-of-inertia tensor In a basis where

$$N^{ab} = \mathrm{diag}\left(N^1, N^2, N^3\right); \tag{14.2.8}$$

we have

$$I^{ab} = \mathrm{diag}\left(N^2 + N^3, N^1 + N^3, N^1 + N^2\right). \tag{14.2.9}$$

Setting $N^1 = N^2 = 0$,

$$I^{ab} = \mathrm{diag}\left(N^3, N^3, 0\right). \tag{14.2.10}$$

In turn,

$$H = \frac{1}{2N^3}\left\{\left(\mathcal{J}^1\right)^2 + \left(\mathcal{J}^2\right)^2\right\} = \frac{1}{2N^3}\left\{\vec{\mathcal{J}}^2 - \left(\mathcal{J}^3\right)^2\right\}. \tag{14.2.11}$$

Commutation Relations We now proceed to compute

$$\begin{aligned}\left[J^a, \mathcal{J}^b\right] &= \left[J^a, J^c R^{cb}\right] = \left[J^a, J^c\right] R^{cb} + J^c\left[J^a, R^{cb}\right] &(14.2.12)\\ &= i\epsilon^{acd} J^d R^{cb} + i\epsilon^{acd} J^c R^{db} &(14.2.13)\\ &= i\epsilon^{acd}(J^d R^{cb} - J^d R^{cb}). &(14.2.14)\end{aligned}$$

In other words

$$\left[J^a, \mathcal{J}^b\right] = 0. \tag{14.2.15}$$

In particular, J^3 and $\mathcal{J}^3$ are compatible observables. Next,

$$\begin{aligned}\left[\mathcal{J}^a, \mathcal{J}^b\right] &= \left[\mathcal{J}^a, J^c R^{cb}\right] = \left[\mathcal{J}^a, J^c\right] R^{cb} + J^c\left[\mathcal{J}^a, R^{cb}\right] &(14.2.16)\\ &= \left[\mathcal{J}^a, J^c R^{cb}\right] = J^c\left[J^e R^{ea}, R^{cb}\right] = J^c\left[J^e, R^{cb}\right] R^{ea} &(14.2.17)\\ &= i\epsilon^{ecd} J^c R^{db} R^{ea} = -iJ^c R^{cd}\epsilon^{abd}. &(14.2.18)\end{aligned}$$

We have arrived at the commutation relations for the $\mathcal{J}$s; they obey an angular-momentum-like Lie algebra:

$$\left[-\mathcal{J}^a, -\mathcal{J}^b\right] = i\epsilon^{abc}(-\mathcal{J}^c). \tag{14.2.19}$$

Note, however, they are scalars under rotation because of eq. (14.2.15). On the other hand, because rotations are orthogonal transformations,

$$\vec{J}^2 \equiv J^a J^a = \mathcal{J}^a \mathcal{J}^a \equiv \vec{\mathcal{J}}^2. \tag{14.2.20}$$

To sum: The $\{\vec{\mathcal{J}}^2 = \vec{J}^2, \mathcal{J}^3, J^3\}$ form a set of mutually compatible observables; with the Lie algebras of J^is and $-\mathcal{J}^i$s both obeying that of the 3D angular momenta. Their simultaneous eigenstates are

$$\begin{aligned}\vec{J}^2\left|J\ M\ K\right\rangle = \vec{\mathcal{J}}^2\left|J\ M\ K\right\rangle = J(J+1)\left|J\ M\ K\right\rangle, &(14.2.21)\\ J^3\left|J\ M\ K\right\rangle = M\left|J\ M\ K\right\rangle, \qquad \text{and} \qquad \mathcal{J}^3\left|J\ M\ K\right\rangle = K\left|J\ M\ K\right\rangle; &(14.2.22)\\ -J \le M, K \le +J, \qquad M, K \text{ independent.} &(14.2.23)\end{aligned}$$

Choosing a basis where $I^{ab} = \mathrm{diag}(I^x, I^y, I^z)$ is diagonal,

$$\begin{aligned}H &= \frac{(\mathcal{J}^x)^2}{2I^x} + \frac{(\mathcal{J}^y)^2}{2I^y} + \frac{(\mathcal{J}^z)^2}{2I^z} &(14.2.24)\\ &= A\vec{\mathcal{J}}^2 + B(\mathcal{J}^z)^2 + C\left((\mathcal{J}^x)^2 - (\mathcal{J}^y)^2\right) &(14.2.25)\\ A &= \frac{1}{4I^x} + \frac{1}{4I^y}, \qquad B = \frac{1}{2I^z} - \frac{1}{4I^x} - \frac{1}{4I^y}, \qquad C = \frac{1}{4I^x} - \frac{1}{4I^y} &(14.2.26)\end{aligned}$$

Additionally,

$$(\mathcal{J}^x)^2 - (\mathcal{J}^y)^2 = \frac{1}{2}\left(\mathcal{J}^+\right)^2 + \frac{1}{2}\left(\mathcal{J}^-\right)^2 \tag{14.2.27}$$

$$\mathcal{J}^\pm \equiv \mathcal{J}^1 \pm i\mathcal{J}^2. \tag{14.2.28}$$

Energy estimates From eq. (14.2.24) and the definition that $I^i \sim$ (mass) $\times$ (inter-atom separation distance)^2, we may estimate the rotation energy levels of a molecule to go as

$$E \sim (m_{\rm N} a^2)^{-1}, \tag{14.2.29}$$

where $m_{\rm N}$ is the typical mass of the nucleus (since that's what dominates the mass of individual atoms) and a is the typical size of the molecule itself.

Problem 14.4. Explain why

$$\vec{\mathcal{J}}^2 = \sum_{J=1}^{\infty} \sum_{-J\leq M,K\leq J} J(J+1)\,|J\ M\ K\rangle\,\langle J\ M\ K|\,, \tag{14.2.30}$$

$$(\mathcal{J}^3)^2 = \sum_{J=1}^{\infty} \sum_{-J\leq M,K\leq J} K^2\,|J\ M\ K\rangle\,\langle J\ M\ K|\,, \tag{14.2.31}$$

$$(\mathcal{J}^\pm)^2 = \sum_{J=1}^{\infty} \sum_{-J\leq M,K\leq J} \sqrt{J(J+1)-(K\pm 1)(K\pm 2)}\sqrt{J(J+1)-K(K\pm 1)} \times |J\ M\ K\pm 2\rangle\,\langle J\ M\ K|\,. \tag{14.2.32}$$

Then use these results to diagonalize the Hamiltonian in eq. (14.2.24) for $J = 1$. □

Problem 14.5. Toy model for triatomic molecule Find the rotational energy levels of the tri-atomic molecular system in Problem (14.2) for a state where $\vec{J}^2\,|J=1\rangle = \vec{\mathcal{J}}^2\,|J=1\rangle = 2\,|J=1\rangle$. □

Wavefunctions See Weinberg for now.

15 Entanglement & Bell's Inequalities: Spin-Half Systems; EPR Paradox

One of the key features of quantum mechanics that distinguishes it from its classical counterpart, is the probabilistic character of its predictions. As we will now explore, the probabilistic character of quantum mechanics is not mere randomness nor simply correlation – but *entanglement*. We shall do so, following Sakurai and Napolitano [3], within the context of spin-half systems, which involves the angular momentum generators

$$S^i = \frac{\sigma^i}{2}. \tag{15.0.1}$$

In the representation where σ^3 is diagonal, the Pauli operators have the matrix representation

$$\widehat{\sigma}^1 \equiv \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \qquad \widehat{\sigma}^2 \equiv \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \qquad \widehat{\sigma}^3 \equiv \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{15.0.2}$$

Suppose we begin with a spin-0 system, which then decays into two distinguishable spin-1/2 particles. This means we may write our state as $\left|0\ 0; \frac{1}{2}\ \frac{1}{2}\right\rangle$ and decompose it into the eigenstates of the spin operators $\widehat{n} \cdot \vec{S}'$ and $\widehat{n} \cdot \vec{S}''$ associated with the two decay products along the unit radial direction $\widehat{n}$.

$$\widehat{n}(\theta, \phi) \equiv (\sin(\theta)\cos(\phi), \sin(\theta)\sin(\phi), \cos(\theta)) \tag{15.0.3}$$

From the rules of addition of angular momentum, we may express the decay through the equation

$$\left|0\ 0; \frac{1}{2}\ \frac{1}{2}\right\rangle = \frac{1}{\sqrt{2}} \left(|\widehat{n}+\rangle \otimes |\widehat{n}-\rangle - |\widehat{n}-\rangle \otimes |\widehat{n}+\rangle\right), \tag{15.0.4}$$

where the first and second slots refers respectively to the first and second decay product. We will further suppose particle 1 and 2 flies off in opposite directions, so that we may measure their spins along some chosen directions, once they have become well separated in space. The possible outcomes of such a thought experiment would illustrate what quantum entanglement is, and why it is a distinct concept from mere correlations.

Problem 15.1. If $|\widehat{z}, 1\rangle \equiv |\widehat{z}+\rangle$ and $|\widehat{z}, 2\rangle \equiv |\widehat{z}-\rangle$ denotes the spin 'up' and 'down' states along the $\widehat{z} = (0, 0, 1)$ direction, verify that the eigenstates of $\widehat{n} \cdot \vec{S} \equiv \widehat{n}^i S^i$ are

$$\xi^{+}{}_{\mathrm{A}}\left(\widehat{n}\right) \equiv \langle \widehat{z}, \mathrm{A} | \, \widehat{n}+\rangle = \left(e^{-i\phi}\cos\left(\theta/2\right), \sin\left(\theta/2\right)\right)^{\mathrm{T}} \tag{15.0.5}$$

and

$$\xi^{-}{}_{\mathrm{A}}\left(\widehat{n}\right) \equiv \langle \widehat{z}, \mathrm{A} | \, \widehat{n}-\rangle = \left(-e^{-i\phi}\sin\left(\theta/2\right), \cos\left(\theta/2\right)\right)^{\mathrm{T}}; \tag{15.0.6}$$

and that they obey the eigen-equation

$$\left(\widehat{n} \cdot \vec{S}\right) \xi^{\pm} = \pm \frac{1}{2} \xi^{\pm}. \tag{15.0.7}$$

According to equations (15.0.5) and (15.0.6),

$$\sum_{\mathrm{A}=\pm} |\widehat{z}, \mathrm{A}\rangle \begin{bmatrix} e^{-i\phi}\cos\left(\theta/2\right) & -e^{-i\phi}\sin\left(\theta/2\right) \\ \sin\left(\theta/2\right) & \cos\left(\theta/2\right) \end{bmatrix}^{\mathrm{A}}{}_{\mathrm{B}} \equiv \sum_{\mathrm{A}=\pm} |\widehat{z}, \mathrm{A}\rangle \, U^{\mathrm{A}}{}_{\mathrm{B}} = |\widehat{n}, \mathrm{B}\rangle \, . \tag{15.0.8}$$

Verify that the inverse relationship is

$$|\widehat{z}, +\rangle = e^{i\phi}\cos\left(\theta/2\right)|\widehat{n}, +\rangle - e^{i\phi}\sin\left(\theta/2\right)|\widehat{n}, -\rangle \, , \tag{15.0.9}$$

$$|\widehat{z}, -\rangle = \sin\left(\theta/2\right)|\widehat{n}, +\rangle + \cos\left(\theta/2\right)|\widehat{n}, -\rangle \, . \tag{15.0.10}$$

We will employ these results in the discussion on entanglement below. □

Measurements Suppose the $\vec{S}\cdot\widehat{z}$ of the first particle is measured, and it is found to be $+1/2$. Then we know that the state of the system must be $|\widehat{z},+\rangle$. If, now, the 2nd particle's $\widehat{S}\cdot\widehat{n}$ is measured. According to eq. (15.0.10),

$$|\widehat{z},+\rangle\otimes|\widehat{z},-\rangle=\sin(\theta/2)\,|\widehat{z},+\rangle\otimes|\widehat{n},+\rangle+\cos(\theta/2)\,|\widehat{z},+\rangle\otimes|\widehat{n},-\rangle\,. \tag{15.0.11}$$

That means the probability of obtaining $+1/2$ for the 2nd particle's $\vec{S}\cdot\widehat{n}$ is $\sin^2(\theta/2)$ and the probability of $-1/2$ is $\cos^2(\theta/2)$.

On the other hand, if the first particle's $\vec{S}\cdot\widehat{z}$ were measured, and it were instead found to be $-1/2$. Then according to eq. (15.0.9), the state becomes

$$|\widehat{z},-\rangle\otimes|\widehat{z},+\rangle=e^{i\phi}\cos(\theta/2)\,|\widehat{z},-\rangle\otimes|\widehat{n},+\rangle-e^{i\phi}\sin(\theta/2)\,|\widehat{z},-\rangle\otimes|\widehat{n},-\rangle\,. \tag{15.0.12}$$

If the $\vec{S}\cdot\vec{n}$ of the 2nd particle is then measured, the probability of obtaining $+1/2$ is $\cos^2(\theta/2)$ and $-1/2$ is $\sin^2(\theta/2)$.

Problem 15.2. Suppose we now have

$$\widehat{n}\equiv(\sin\theta\cos\phi,\sin\theta\sin\phi,\cos\theta)\,, \tag{15.0.13}$$
$$\widehat{n}'\equiv(\sin\theta'\cos\phi',\sin\theta'\sin\phi',\cos\theta')\,. \tag{15.0.14}$$

Use equations (15.0.9) and (15.0.10) to verify, the singlet state in eq. (15.0.4) can be expressed as

$$\begin{aligned}\left|0\ 0;\frac{1}{2}\ \frac{1}{2}\right\rangle=&\frac{1}{\sqrt{2}}\,|\widehat{n}+\rangle\otimes|\widehat{n}'+\rangle\,e^{i\phi'}\left(e^{i(\phi-\phi')}\cos(\theta/2)\sin(\theta'/2)-\cos(\theta'/2)\sin(\theta/2)\right)\\&+\frac{1}{\sqrt{2}}\,|\widehat{n}+\rangle\otimes|\widehat{n}'-\rangle\,e^{i\phi'}\left(e^{i(\phi-\phi')}\cos(\theta/2)\cos(\theta'/2)+\sin(\theta'/2)\sin(\theta/2)\right)\\&-\frac{1}{\sqrt{2}}\,|\widehat{n}-\rangle\otimes|\widehat{n}'+\rangle\,e^{i\phi}\left(e^{i(\phi'-\phi)}\cos(\theta/2)\cos(\theta'/2)+\sin(\theta'/2)\sin(\theta/2)\right)\\&+\frac{1}{\sqrt{2}}\,|\widehat{n}-\rangle\otimes|\widehat{n}'-\rangle\,e^{i\phi}\left(e^{i(\phi'-\phi)}\cos(\theta/2)\sin(\theta'/2)-\cos(\theta'/2)\sin(\theta/2)\right).\end{aligned} \tag{15.0.15}$$

Write down the probabilities $P(\widehat{n}+,\widehat{n}'+)$, $P(\widehat{n}+,\widehat{n}'-)$, $P(\widehat{n}-,\widehat{n}'+)$, and $P(\widehat{n}-,\widehat{n}'-)$. Since the coordinate system is arbitrary, and since there are only two vectors in this problem, you may assume they both lie on the $(1,3)$ plane; use this observation to show that all these probabilities depend only on the angle θ between $\widehat{n}$ and $\widehat{n}'$; namely, $\theta=\arccos(\widehat{n}\cdot\widehat{n}')$. □

Bell's Inequality How does particle 2 'know' what was being measured at particle 1? Once particle 1's $\widehat{z}\cdot\vec{S}$ is measured to be $+1/2$, for instance, then the $\widehat{z}\cdot\vec{S}$ of particle 2 must turn out to be $-1/2$ – even if the time difference in the measurements of particles 1 and 2 were shorter than the light crossing time between them. More generally, equations (15.0.11) and (15.0.12) indicate the probability of measuring 'up' or 'down' for particle 2's spin component along some direction $\widehat{n}'$ depends (instaneously) on how it is oriented relative to the spin direction measured for particle 1. This apparent instant 'action-at-a-distance' makes many physicists – including Einstein himself – very uncomfortable, because it does not sit well with relativity.

Is it possible for a 'local' theory to reproduce the predictions of quantum mechanics? Suppose such a theory is able to produce *seemingly* probabilistic outcomes of spin, consistent with the predictions of quantum mechanics. We will remain agnostic about the underlying mechanism of how it produces outcomes that *appears* random; but we will assume the outcome is already fixed once the initial spin-0 particle decays. This is to ensure the theory is a 'local' one: for, if the outcome were not already predetermined, it would mean the measurement process somehow allows for a instantaneous influence-at-a-distance (for e.g., observing $\widehat{z}+$ for particle 1 immediately causes $\widehat{z}-$ for particle 2). As we shall see, this 'Einstein locality principle' leads us to inequalities (named after its discoverer John Bell) involving the probabilities of obtaining various results that are in fact violated by quantum mechanics itself. In other words, there are observable differences between such 'local' theories and quantum mechanics.

To see this, we need to consider three distinct detector orientations, which we shall denote $\widehat{a}$, $\widehat{b}$, and $\widehat{c}$. Such local theories, in order to be consistent with quantum mechanics, do not allow simultaneous measurements of spin along different directions. However, we shall assume that particle 1 (and 2), when produced, will lead to definite outcomes for the spins measured along $\widehat{a}$, $\widehat{b}$, and $\widehat{c}$. Let's say out of a total N events, N_1 produce particle 1 with the definite outcome $\widehat{a}+, \widehat{b}+, \widehat{c}+$ and particle 2 with definition outcome $\widehat{a}-, \widehat{b}-, \widehat{c}-$; N_2 with $\widehat{a}+, \widehat{b}+, \widehat{c}-$ and $\widehat{a}-, \widehat{b}-, \widehat{c}+$; etc – so that $N = \sum_i N_i$. (Note that the sum of particle 1 and 2's spin components must be zero; so we actually really only need to specify particle 1's outcome.)

No. of events	Decay Particle 1	Decay Particle 2
N_1	$\widehat{a}+, \widehat{b}+, \widehat{c}+$	$\widehat{a}-, \widehat{b}-, \widehat{c}-$
N_2	$\widehat{a}+, \widehat{b}+, \widehat{c}-$	$\widehat{a}-, \widehat{b}-, \widehat{c}+$
N_3	$\widehat{a}+, \widehat{b}-, \widehat{c}+$	$\widehat{a}-, \widehat{b}+, \widehat{c}-$
N_4	$\widehat{a}+, \widehat{b}-, \widehat{c}-$	$\widehat{a}-, \widehat{b}+, \widehat{c}+$
N_5	$\widehat{a}-, \widehat{b}+, \widehat{c}+$	$\widehat{a}+, \widehat{b}-, \widehat{c}-$
N_6	$\widehat{a}-, \widehat{b}+, \widehat{c}-$	$\widehat{a}+, \widehat{b}-, \widehat{c}+$
N_7	$\widehat{a}-, \widehat{b}-, \widehat{c}+$	$\widehat{a}+, \widehat{b}+, \widehat{c}-$
N_8	$\widehat{a}-, \widehat{b}-, \widehat{c}-$	$\widehat{a}+, \widehat{b}+, \widehat{c}+$

We may see that the probability of obtaining spin up along $\widehat{a}$ for particle 1; and spin up along $\widehat{b}$ for particle 2 is

$$P(\widehat{a}+\widehat{b}+) = \frac{N_3+N_4}{\sum_{i=1}^{8} N_i} \equiv \frac{N_3+N_4}{N}; \tag{15.0.16}$$

while the probability for spin up along $\widehat{a}$ for 1 and spin up along $\widehat{c}$ for 2 is

$$P(\widehat{a}+\widehat{c}+) = \frac{N_2+N_4}{N}; \tag{15.0.17}$$

and probability for spin up along $\widehat{c}$ for 1 and $\widehat{b}$ for 2 is

$$P(\widehat{a}+\widehat{c}+) = \frac{N_3+N_7}{N}. \tag{15.0.18}$$

Since the $\{N_i\}$ are non-negative, and hence $N_3 + N_4 \leq N_2 + N_3 + N_4 + N_7$, this hands us an example of Bell's inequalities:

$$P(\widehat{a}+, \widehat{b}+) \leq P(\widehat{a}+, \widehat{c}+) + P(\widehat{c}+, \widehat{b}+). \tag{15.0.19}$$

See Sakurai [3] eq. (3.10.9), and the more detailed discussion that led up to it.

Problem 15.3. For simplicity, assume $\widehat{a}$, $\widehat{b}$ and $\widehat{c}$ all lie on the $(1,3)$ plane; and let θ_1 denote the angle between $\widehat{a}$ and $\widehat{b}$ and θ_2 denote the angle between $\widehat{a}$ and $\widehat{c}$. (Note: $\theta_1 \in [0,\pi]$ and $\theta_2 \in [0,\pi]$.) Compute $P(\widehat{a}+, \widehat{b}+)$, $P(\widehat{a}+, \widehat{c}+)$, and $P(\widehat{c}+, \widehat{b}+)$ in accordance to quantum mechanics, and figure out what region on the (θ_1, θ_2) Bell's inequality is violated. Hint: See Problem (15.2).

Bonus: Can you find a Bell's inequality different from that in eq. (15.0.19)? That is, find probabilities for different set of observables (e.g., $(\widehat{a}+, \widehat{b}-)$, $(\widehat{a}-, \widehat{b}+)$, $(\widehat{c}+, \widehat{b}-)$, etc.) that satisfy their own inequalities. Does it get violated by quantum mechanics? □

Correlation vs Quantum Entanglement Why did we have to examine the case where there are three distinct detector orientations? Suppose we had only examined the probability of obtaining $P(\widehat{a}+\widehat{b}+)$, $P(\widehat{a}+\widehat{b}-)$, $P(\widehat{a}-\widehat{b}+)$, and $P(\widehat{a}-\widehat{b}-)$. Let us again assume we had a theory that *appears* probabilistic but is local in the sense that, once the decay particles 1 and 2 have been produced, their states are fixed. We may then draw a table of outcomes as we did before; where $N_{i\in\{1,2,3,4\}}$ is the number of events that yield the spin results of particles 1 and 2 displayed in the corresponding 2nd and 3rd columns.

No. of events	Decay Particle 1	Decay Particle 2	Probability	Probability
N_1	$\widehat{a}+, \widehat{b}+$	$\widehat{a}-, \widehat{b}-$	$P(\widehat{a}+, \widehat{b}-)$	$P(\widehat{b}+, \widehat{a}-)$
N_2	$\widehat{a}+, \widehat{b}-$	$\widehat{a}-, \widehat{b}+$	$P(\widehat{a}+, \widehat{b}+)$	$P(\widehat{b}-, \widehat{a}-)$
N_3	$\widehat{a}-, \widehat{b}+$	$\widehat{a}+, \widehat{b}-$	$P(\widehat{a}-, \widehat{b}-)$	$P(\widehat{b}+, \widehat{a}+)$
N_4	$\widehat{a}-, \widehat{b}-$	$\widehat{a}+, \widehat{b}+$	$P(\widehat{a}-, \widehat{b}+)$	$P(\widehat{b}-, \widehat{a}+)$

Table (15).

Because there are only 2 spin orientations considered here, we see that each possible outcome is associated with a distinct probability. Contrast this with the 3 orientation case above, where $P(\widehat{a}+\widehat{b}+)$, $P(\widehat{a}+\widehat{c}+)$, and $P(\widehat{c}+\widehat{b}+)$ involved more than one N_i each. Therefore, in this 2 detector orientations case, if the underlying theory is able to produce the same probabilities you've computed in Problem (15.2), then it would be indistinguishable from quantum mechanics – as far as this simple system is concerned.

Problem 15.4. Identify the $N_{i\in\{1,2,3,4\}}$ in Table (15) with the probabilities computed in Problem (15.2). □

Einstein–Podolsky–Rosen(-Bohm) Paradox & Causality What we have just witnessed is the *entanglement* between the spin properties of particle 1 and 2, produced upon the decay of the original spin 0 object.

16 Path Integrals

Path integrals, sometimes also known as functional integrals, provide an alternate (but equivalent) formulation of quantum mechanics. This was pioneered by Richard Feynman as part of his PhD thesis.[11] Path integration is usually not the most practical way to solve quantum mechanical problems, but the perspective it offers is quite distinct from the Schrödinger-Heisenberg one – one no longer deals with operators and the recovery of classical mechanics follows almost immediately from the stationary phase approximation. Also, in Quantum Field Theory (QFT), path integrals become an essential tool when dealing with the quantization of gauge theories.[12]

As we will demonstrate, the key object is the quantum mechanical amplitude for a particle to propagate from $(t', \vec{x}')$ to $(t, \vec{x})$:

$$\langle \vec{x} \,|U(t,t')|\, \vec{x}' \rangle = \int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q} \int \mathcal{D}\vec{p} \exp\left[i \int_{t'}^{t} \Big(\vec{p}(s) \cdot \dot{\vec{q}}(s) - H\left(\vec{q}(s), \vec{p}(s)\right) \Big) \, \mathrm{d}s \right], \tag{16.0.1}$$

where U is the unitary time-evolution operator which obeys Schrödinger's equation

$$i\partial_t U(t,t') = HU(t,t') \tag{16.0.2}$$

with the initial condition

$$U(t=t') = \mathbb{I}. \tag{16.0.3}$$

The right hand side of eq. (16.0.1) is an integration over all possible trajectories $\{\vec{q}(s)\}$ – hence, *path integration* – that begins at $(t', \vec{x}')$ and ends at $(t, \vec{x})$. The integration over $\vec{p}$ is unconstrained. The $\vec{q}$ is the position coordinate; $\vec{p}$ is its momentum; and H is the Hamiltonian of the dynamics. That the quantum mechanical amplitude is phrased as the sum over all possible paths, i.e., Feynman's formulation of quantum mechanics, is to be contrasted against the perspective of the usual Schrödinger's wave function.

Problem 16.1. If $K(t, \vec{x}; t', \vec{x}')$ is the quantum mechanical amplitude (aka path integral) from $(t', \vec{x}')$ to $(t, \vec{x})$,

$$K(t, \vec{x}; t', \vec{x}') \equiv \langle \vec{x} \,|U(t,t')|\, \vec{x}' \rangle \,; \tag{16.0.4}$$

explain why

$$(i\partial_t - H)\, G^+(t, \vec{x}; t', \vec{x}') = i\delta(t-t')\delta^{(D)}(\vec{x} - \vec{x}'), \tag{16.0.5}$$

if

$$G^+(t, \vec{x}; t', \vec{x}') \equiv \Theta(t-t') K(t, \vec{x}; t', \vec{x}'). \tag{16.0.6}$$

Here, $\Theta(z) = 1$ for $z > 0$ and $= 0$ for $z < 0$. □

[11] Norbert Wiener came up with the Euclidean version of the path integral before Feynman.

[12] Some books dedicated to path integrals are: Feynman and Hibbs [4]; Schulman [5]; and Kleinert [6].

Lagrangian mechanics As is often the case, the H is quadratic in momentum; for e.g.,

$$H(\vec{q},\vec{p}) = \frac{\vec{p}^2}{2} + V(\vec{q}). \tag{16.0.7}$$

[13]We may 'complete-the-square' within the exponent $\vec{p}\cdot\dot{\vec{q}} - H$,

$$\vec{p}\cdot\dot{\vec{q}} - \frac{\vec{p}^2}{2} - V(\vec{q}) = -\left(\frac{\vec{p}}{\sqrt{2}} - \sqrt{2}\frac{\dot{\vec{q}}}{2}\right)^2 + 2\frac{\dot{\vec{q}}^2}{4} - V(\vec{q}) \tag{16.0.8}$$

$$= -\left(\frac{\vec{p}}{\sqrt{2}} - \sqrt{2}\frac{\dot{\vec{q}}}{2}\right)^2 + \frac{1}{2}\dot{\vec{q}}^2 - V(\vec{q}). \tag{16.0.9}$$

The integration over $\vec{p}$ can be recognized as an overall multiplicative factor.

$$\langle \vec{x}\,|U(t,t')|\,\vec{x}'\rangle = \int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q}\int \mathcal{D}\vec{p}\exp\left[i\int_{t'}^{t}\left(\vec{p}(s)\cdot\dot{\vec{q}}(s) - \frac{\vec{p}^2}{2} - V(\vec{q})\right)\mathrm{d}s\right] \tag{16.0.10}$$

$$= \int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q}\int \mathcal{D}\left\{\sqrt{2}\left(\frac{\vec{p}}{\sqrt{2}} - \sqrt{2}\frac{\dot{\vec{q}}}{2}\right)\right\}$$
$$\times\exp\left[i\int_{t'}^{t}\left(-\left(\frac{\vec{p}}{\sqrt{2}} - \sqrt{2}\frac{\dot{\vec{q}}}{2}\right)^2 + \frac{1}{2}\dot{\vec{q}}^2 - V(\vec{q})\right)\mathrm{d}s\right] \tag{16.0.11}$$

$$= \mathcal{N}\int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q}\exp\left[i\int_{t'}^{t}\left(\frac{1}{2}\dot{\vec{q}}^2(s) - V\left(\vec{q}(s)\right)\right)\mathrm{d}s\right]; \tag{16.0.12}$$

where

$$\mathcal{N} \equiv \int \mathcal{D}\left\{\sqrt{2}\vec{p}'\right\}\exp\left[-i\int_{t'}^{t}\vec{p}'^2\mathrm{d}s\right]. \tag{16.0.13}$$

In other words, in many cases of interest, the path integral reduces to one governed by the Lagrangian of the dynamics of the particle.

$$\langle \vec{x}\,|U(t,t')|\,\vec{x}'\rangle = \mathcal{N}\int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q}\exp\left[iS\right], \tag{16.0.14}$$

$$S \equiv \int_{t'}^{t} L\left(\vec{q},\dot{\vec{q}}\right)\mathrm{d}s. \tag{16.0.15}$$

In this sense, we have re-discovered Lagrangian mechanics from the Hamiltonian formulation of quantum mechanics.

[13]We have deliberately set $m = 1$, because the same form of the Hamiltonian appears in relativistic QFT where m does not appear like in the non-relativistic $\vec{p}^2/(2m)$.

16.1 Example: Free Particle in Flat Euclidean Space

We will shortly begin to discuss in more detail what path integration really means. But let us first tackle the simplest such example: the free particle.

$$H(\vec{q},\vec{p}) = \frac{\vec{p}^2}{2m} \qquad \Leftrightarrow \qquad L(\vec{q},\dot{\vec{q}}) = \frac{m}{2}\dot{\vec{q}}^2 \tag{16.1.1}$$

It is possible to evaluate the quantum mechanical amplitude directly. Since H is time-independent here,

$$\left\langle \vec{x} \left| \exp\left[-i\frac{\vec{p}^2}{2m}(t-t')\right] \right| \vec{x}' \right\rangle = \int \frac{\mathrm{d}^D k}{(2\pi)^D} \left\langle \vec{x} \left| \exp\left[-i\frac{\vec{p}^2}{2m}(t-t')\right] \right| \vec{k} \right\rangle \langle \vec{k}|\vec{x}'\rangle \tag{16.1.2}$$

$$= \int \frac{\mathrm{d}^D k}{(2\pi)^D} \exp\left[-i\vec{k}^2\frac{t-t'}{2m} + i\vec{k}\cdot(\vec{x}-\vec{x}')\right] \tag{16.1.3}$$

We can then complete the square

$$\frac{t-t'}{2m}\vec{k}^2 - \vec{k}\cdot(\vec{x}-\vec{x}') = \left\{\sqrt{\frac{t-t'}{2m}}\vec{k} - \frac{1}{2}\sqrt{\frac{2m}{t-t'}}\,(\vec{x}-\vec{x}')\right\}^2 - \frac{m}{2(t-t')}(\vec{x}-\vec{x}')^2 \tag{16.1.4}$$

$$= \frac{t-t'}{2m}\left\{\vec{k} - \frac{1}{2}\frac{2m}{t-t'}\,(\vec{x}-\vec{x}')\right\}^2 - \frac{m}{2(t-t')}(\vec{x}-\vec{x}')^2. \tag{16.1.5}$$

And use analytic continuation of

$$\int_{\mathbb{R}^D} \mathrm{d}^D z \exp[-\mu\vec{z}^2] = (\pi/\mu)^{D/2} \tag{16.1.6}$$

to deduce, for $t-t' > 0$ and $m > 0$,

$$\left\langle \vec{x} \left| \exp\left[-i\frac{\vec{p}^2}{2m}(t-t')\right] \right| \vec{x}' \right\rangle = \exp\left[\frac{im}{2(t-t')}(\vec{x}-\vec{x}')^2\right] e^{-i\frac{\pi}{4}D} \left(\frac{m}{2\pi(t-t')}\right)^{D/2}; \tag{16.1.7}$$

where the square root is the positive one.

Problem 16.2. Explain why, if $\xi > 0$,

$$\int_{\mathbb{R}} \mathrm{d}z \exp(\pm i\xi z^2) = e^{\pm i\frac{\pi}{4}}\sqrt{\frac{\pi}{\xi}}, \tag{16.1.8}$$

where the square root is the positive one. (Hint: this requires complex analysis and Jordan's lemma.) Why does this explain the phase factor $e^{-i\pi D/4}$ in eq. (16.1.9)?

Now explain why, for arbitrary $t-t'$,

$$\left\langle \vec{x} \left| \exp\left[-i\frac{\vec{p}^2}{2m}(t-t')\right] \right| \vec{x}' \right\rangle = \exp\left[\frac{im}{2(t-t')}(\vec{x}-\vec{x}')^2\right] e^{-i\frac{\pi}{4}D\cdot\mathrm{sgn}[t-t']} \left(\frac{m}{2\pi|t-t'|}\right)^{D/2}. \tag{16.1.9}$$

The $\mathrm{sgn}[x] = +1$ whenever $x > 0$; and $\mathrm{sgn}[x] = -1$ whenever $x < 0$. □

We may also start from the path integral itself.

$$\mathcal{N}\int_{\vec{x}'}^{\vec{x}}\mathcal{D}\exp\left[i\int_{t'}^{t}\frac{m}{2}\dot{\vec{q}}^2\mathrm{d}s\right] \tag{16.1.10}$$

We will perform a change-of-variables

$$\vec{q}(s)=\vec{q}_c(s)+\vec{\xi}(s) \tag{16.1.11}$$

such that $\vec{q}_c(s)$ obeys the 'classical trajectory'

$$\ddot{\vec{q}}_c(s)=0, \qquad \vec{q}_c(t')=\vec{x}', \qquad \vec{q}_c(t)=\vec{x}. \tag{16.1.12}$$

In fact, the solution is

$$\vec{q}_c(s)=\vec{x}'+\frac{s-t'}{t-t'}(\vec{x}-\vec{x}'). \tag{16.1.13}$$

Since the $\vec{q}(s)$ in the path integral is defined to go from $(t',\vec{x}')$ to $(t,\vec{x})$, that means the remainder $\vec{\xi}$ has to be subject to the (Dirichlet) boundary conditions

$$\vec{\xi}(t')=\vec{0} \qquad \text{and} \qquad \vec{\xi}(t)=\vec{0}. \tag{16.1.14}$$

Let us focus on the action occurring within the path integral.

$$S=\int_{t'}^{t}\frac{m}{2}\dot{\vec{q}}^2\mathrm{d}s=\int_{t'}^{t}\frac{m}{2}(\dot{\vec{q}}_c+\dot{\vec{\xi}})^2\mathrm{d}s \tag{16.1.15}$$

Using eq. (16.1.12),

$$S=\int_{t'}^{t}\frac{m}{2}\dot{\vec{q}}^2\mathrm{d}s=\int_{t'}^{t}\frac{m}{2}\left(\left(\frac{\vec{x}-\vec{x}'}{t-t'}\right)^2+2\dot{\vec{q}}_c\cdot\dot{\vec{\xi}}+\dot{\vec{\xi}}^2\right)\mathrm{d}s \tag{16.1.16}$$

$$=\frac{m}{2}\frac{(\vec{x}-\vec{x}')^2}{t-t'}+\frac{m}{2}\left[2\dot{\vec{q}}_c\cdot\vec{\xi}\right]_{t'}^{t}+\frac{m}{2}\int_{t'}^{t}\left(-2\ddot{\vec{q}}_c\cdot\vec{\xi}+\dot{\vec{\xi}}^2\right)\mathrm{d}s. \tag{16.1.17}$$

We have integrated-by-parts the second term within the integral because, according to the boundary conditions in eq. (16.1.14) obeyed by the $\vec{\xi}$, the surface terms actually vanish. Moreover, the classical ODE obeyed by $\vec{q}_c$ (cf. eq. (16.1.12)) also eliminates the $\ddot{\vec{q}}_c\cdot\vec{\xi}$ term.

$$S=\frac{m}{2}\frac{(\vec{x}-\vec{x}')^2}{t-t'}+\frac{m}{2}\int_{t'}^{t}\dot{\vec{\xi}}^2\mathrm{d}s. \tag{16.1.18}$$

To sum: the action occurring within the free particle path integral receives two contributions, one 'classical' portion (the first term on the RHS) due to a particle obeying constant acceleration moving from $(t',\vec{x}')$ to $(t,\vec{x})$; and another 'quantum' portion that propagates from $(t',\vec{0})$ to $(t,\vec{0})$. Note that since $\vec{q}_c$ is a fixed (i.e., classical) trajectory, it is a constant as far as the integration over paths is concerned:

$$\mathcal{D}\vec{q}=\mathcal{D}\vec{\xi}. \tag{16.1.19}$$

At this point, inserting eq. (16.1.18) into the right hand side of eq. (16.0.14), our path integral is

$$\left\langle \vec{x} \left| \exp\left[-i\frac{\vec{p}^2}{2m}(t-t')\right] \right| \vec{x}' \right\rangle = \mathcal{N}' \exp\left[\frac{im}{2}\frac{(\vec{x}-\vec{x}')^2}{t-t'}\right] \tag{16.1.20}$$

$$\mathcal{N}' \equiv \mathcal{N} \int_{\vec{0}}^{\vec{0}} \mathcal{D}\vec{\xi} \exp\left[i\frac{m}{2}\int_{t'}^{t} \dot{\vec{\xi}}^2 \mathrm{d}s\right]. \tag{16.1.21}$$

We may in fact determine $\mathcal{N}'$ – without directly evaluating the $\left\langle \vec{0} \left| U \right| \vec{0} \right\rangle$ – up to an overall multiplicative phase by recalling the transition amplitude may be regarded as the matrix element of the unitary time evolution operator. In particular,

$$\delta^{(D)}(\vec{x}-\vec{y}) = \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x}' \left\langle \vec{x} \left| \exp\left[-i\frac{\vec{p}^2}{2m}(t-t')\right] \right| \vec{x}' \right\rangle \overline{\left\langle \vec{y} \left| \exp\left[-i\frac{\vec{p}^2}{2m}(t-t')\right] \right| \vec{x}' \right\rangle} \tag{16.1.22}$$

$$= \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x}' |\mathcal{N}'[t,t']|^2 \exp\left[\frac{im}{2}\frac{(\vec{x}-\vec{x}')^2-(\vec{y}-\vec{x}')^2}{t-t'}\right] \tag{16.1.23}$$

$$= |\mathcal{N}'[t,t']|^2 \exp\left[\frac{im}{2(t-t')}(\vec{x}^2-\vec{y}^2)\right] \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x}' e^{-i(\vec{x}-\vec{y})\cdot\vec{x}'\frac{m}{t-t'}}. \tag{16.1.24}$$

Recalling the integral representation of the Dirac delta-function, we arrive at

$$|\mathcal{N}'| = \left(\frac{m}{2\pi(t-t')}\right)^{D/2}. \tag{16.1.25}$$

At this point, we gather from eq. (16.1.20),

$$\left\langle \vec{x} \left| \exp\left[-i\frac{\vec{p}^2}{2m}(t-t')\right] \right| \vec{x}' \right\rangle = e^{i\delta(t,t')} \left(\frac{m}{2\pi(t-t')}\right)^{D/2} \exp\left[\frac{im}{2}\frac{(\vec{x}-\vec{x}')^2}{t-t'}\right] \tag{16.1.26}$$

Comparison between equations (16.1.9) and (16.1.26) allows us to see that the exponent $\exp(i\frac{m}{2(t-t')}(\vec{x}-\vec{x}')^2)$ in the former comes entirely from the classical trajectory; and also lets us identify the phase to be

$$\exp(i\delta(t,t')) = e^{-i\frac{\pi}{4}D}. \tag{16.1.27}$$

Recall from eq. (16.0.14) that, up to an overall multiplicative factor,

$$\int_{\vec{0}}^{\vec{0}} \mathcal{D}\vec{\xi} \exp\left[i\frac{m}{2}\int_{t'}^{t} \dot{\vec{\xi}}^2 \mathrm{d}s\right] \propto \left\langle \vec{0} \left| U(t,t') \right| \vec{0} \right\rangle \tag{16.1.28}$$

$$= \left\langle \vec{0} \left| \exp\left(-i\frac{\vec{p}^2}{2m}(t-t')\right) \right| \vec{0}' \right\rangle. \tag{16.1.29}$$

This is of course what we did earlier, but now with $\vec{x} = \vec{x}' = \vec{0}$. In fact, we may re-write eq. (16.1.9) as

$$\left\langle \vec{x} \left| \exp\left[-i\frac{\vec{p}^2}{2m}(t-t')\right] \right| \vec{x}' \right\rangle = \exp\left[\frac{im}{2(t-t')}(\vec{x}-\vec{x}')^2\right] \left\langle \vec{0} \left| \exp\left[-i\frac{\vec{p}^2}{2m}(t-t')\right] \right| \vec{0} \right\rangle,$$

$$\left\langle \vec{0} \left| \exp\left[-i\frac{\vec{p}^2}{2m}(t-t')\right] \right| \vec{0} \right\rangle = e^{-i\frac{\pi}{4}D} \left(\frac{m}{2\pi(t-t')}\right)^{D/2} \propto \int_{\vec{0}}^{\vec{0}} \mathcal{D}\vec{\xi} \exp\left[i\frac{m}{2}\int_{t'}^{t} \dot{\vec{\xi}}^2 \mathrm{d}s\right]. \tag{16.1.30}$$

16.2 Path Integrals From Time-Independent Hamiltonians

We now turn to a more systematic derivation of the path integral

$$\left\langle \vec{x} \left| e^{-iH(t-t')} \right| \vec{x}' \right\rangle = \int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q} \int \mathcal{D}\vec{p} \exp\left[i \int_{t'}^{t} \mathrm{d}s \left(\vec{p} \cdot \dot{\vec{q}} - H\left[\vec{p}(s), \vec{q}(s) \right] \right) \right]. \tag{16.2.1}$$

For technical simplicity we will assume H is time independent; we will also set the mass of the particle to unity for technical convenience. The time independence of H means we may write the quantum transition amplitude in eq. (16.2.1) as

$$\begin{aligned} \left\langle \vec{x} \left| e^{-iH(t-t')} \right| \vec{x}' \right\rangle &= \lim_{N\to\infty} \left\langle \vec{x} \left| e^{-iH(\delta t_N + \delta t_{N-1} + \cdots + \delta t_2 + \delta t_1)} \right| \vec{x}' \right\rangle, \qquad \delta t_1 + \cdots + \delta t_N \equiv t - t' \\ &= \lim_{N\to\infty} \int_{\mathbb{R}^D} \mathrm{d}^D \vec{q}_N \ldots \mathrm{d}^D \vec{q}_2 \left\langle \vec{x} \left| e^{-iH\delta t_N} \right| \vec{q}_N \right\rangle \left\langle \vec{q}_N \left| e^{-iH\delta t_{N-1}} \right| \vec{q}_{N-1} \right\rangle \\ &\times \left\langle \vec{q}_{N-1} \left| e^{-iH\delta t_{N-2}} \right| \vec{q}_{N-2} \right\rangle \ldots \left\langle \vec{q}_3 \left| e^{-iH\delta t_2} \right| \vec{q}_2 \right\rangle \left\langle \vec{q}_2 \left| e^{-iH\delta t_1} \right| \vec{x}' \right\rangle. \end{aligned} \tag{16.2.2}$$

(All the time intervals are equal $\delta t_i \equiv \delta t$, but we put a label on them to help us distinguish between the exponential factors arising from the different time slices.) Now, we will assume that the position and momentum operators ($\vec{X}$ and $\vec{P}$) within H has been arranged such that

$$\left\langle \vec{q} \left| H\left(\vec{X}, \vec{P} \right) \right| \vec{k} \right\rangle = H\left(\vec{q}, \vec{k} \right) \left\langle \vec{q} \middle| \vec{k} \right\rangle. \tag{16.2.3}$$

This is not always true, but is certainly so for the common form of the Hamiltonian

$$H = \frac{1}{2}\vec{P}^2 + V(\vec{X}). \tag{16.2.4}$$

With this assumption, and up to order δt,

$$\begin{aligned} &\left\langle \vec{q}_{i+1} \left| e^{-iH\delta t_i} \right| \vec{q}_i \right\rangle \\ &= \left\langle \vec{q}_{i+1} \left| 1 - iH\left(\vec{X}, \vec{P} \right) \delta t_i + \mathcal{O}(\delta t^2) \right| \vec{q}_i \right\rangle && (16.2.5) \\ &= \int \frac{\mathrm{d}^D \vec{k}_i}{(2\pi)^D} \left\langle \vec{q}_{i+1} \left| 1 - iH\left(\vec{X}, \vec{P} \right) \delta t_i + \mathcal{O}(\delta t^2) \right| \vec{k}_i \right\rangle \left\langle \vec{k}_i \middle| \vec{q}_i \right\rangle && (16.2.6) \\ &= \int \frac{\mathrm{d}^D \vec{k}_i}{(2\pi)^D} \left(1 - iH\left(\vec{q}_{i+1}, \vec{k}_i \right) \delta t_i + \mathcal{O}(\delta t^2) \right) \left\langle \vec{q}_{i+1} \middle| \vec{k}_i \right\rangle \left\langle \vec{k}_i \middle| \vec{q}_i \right\rangle && (16.2.7) \\ &= \int \frac{\mathrm{d}^D \vec{k}_i}{(2\pi)^D} \exp\left(i\vec{k}_i \left(\vec{q}_{i+1} - \vec{q}_i \right) - iH\left(\vec{q}_{i+1}, \vec{k}_i \right) \delta t_i \right). && (16.2.8) \end{aligned}$$

This in turn implies eq. (16.2.2) turns into

$$\begin{aligned} \left\langle \vec{x} \left| e^{-iH(t-t')} \right| \vec{x}' \right\rangle &= \lim_{N\to\infty} \int_{\mathbb{R}^D} \mathrm{d}^D \vec{q}_N \ldots \mathrm{d}^D \vec{q}_2 \int_{\mathbb{R}^D} \frac{\mathrm{d}^D \vec{k}_N}{(2\pi)^D} \ldots \frac{\mathrm{d}^D \vec{k}_1}{(2\pi)^D} \\ &\times e^{i\vec{k}_N \cdot (\vec{x} - \vec{q}_N) - iH(\vec{x}, \vec{k}_N)\delta t_N} e^{i\vec{k}_{N-1} \cdot (\vec{q}_N - \vec{q}_{N-1}) - iH(\vec{q}_N, \vec{k}_{N-1})\delta t_{N-1}} \\ &\times e^{i\vec{k}_{N-2} \cdot (\vec{q}_{N-1} - \vec{q}_{N-2}) - iH(\vec{q}_{N-1}, \vec{k}_{N-2})\delta t_{N-2}} \ldots e^{i\vec{k}_1 \cdot (\vec{q}_2 - \vec{x}') - iH(\vec{q}_2, \vec{k}_1)\delta t_1} \end{aligned} \tag{16.2.9}$$

[14]This is what we mean by the path integration measures $\int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q} \int \mathcal{D}\vec{p}$ in eq. (16.2.1). Notice there is one more momentum than position integration, because there are no constraints on the momentum on the final/initial time slices.

> Provided the operator ordering assumption in eq. (16.2.3) holds, the quantum mechanical transition amplitude for a particle to propagate from $\vec{x}'$ to $\vec{x}$ can be viewed as the limit of the continuous product over all times the exponential $\exp(i\{\vec{p}\cdot\dot{\vec{q}} - H(\vec{q},\vec{p})\}\delta t)$, integrated over all momentum and positions at each time slice – except the end $\vec{q}$s are held fixed at $\vec{x}'$ and $\vec{x}$.

Stationary Phase Approximation & Semi-Classical Limit For an ordinary integral, the Riemann–Lebesgue lemma tells us, if

$$f(x) \equiv \int_a^b \exp(ix\varphi(t))\mathrm{d}t, \tag{16.2.10}$$

where a and b are arbitrary real numbers and $\varphi(t)$ is continuously differentiable and is not constant over a finite region within the interval $t \in [a,b]$. Then

$$f(x \to +\infty) = 0. \tag{16.2.11}$$

We may understand this heuristically. As $x \to \infty$, the exponential oscillates wildly; and we may in fact break the interval $t \in [a,b]$ into small enough segments $t \in [t_i, t_{i+1}]$ so that $\varphi(t)$ is roughly a linear function of t in each of them and such that $[t_i, t_{i+1}]$ corresponds exactly to one period of $\exp(ix\varphi(t)) \approx \exp(ix(a+bt))$. Then,

$$\int_{t_i}^{t_{i+1}} \exp(ix(a+bt))\mathrm{d}t = 0 \tag{16.2.12}$$

as $x \to +\infty$. (This is also why there is a requirement that φ be non-constant everywhere within $t \in [a,b]$; otherwise the exponential will not oscillate there, and there is no period to integrate over to produce a zero result.)

General Formula In this limit as $x \to +\infty$, we may seek the leading behavior of this integral by searching for the point t_0 such that

$$\varphi'(t_0) = 0. \tag{16.2.13}$$

For, in that region the φ is varies slower than first power in t, and

$$\int_a^b \exp(ix\varphi(t))\mathrm{d}t = \int_a^b \exp\left(ix\left\{\varphi(t_0) + \frac{1}{2}\varphi''(t_0)(t-t_0)^2 + \dots\right\}\right)\mathrm{d}t \tag{16.2.14}$$

$$\approx e^{ix\varphi(t_0)} \int_{\mathbb{R}} \exp\left(i(x/2)\varphi''(t_0)\tau^2\right)\mathrm{d}\tau. \tag{16.2.15}$$

[14]There are subtleties related to this 'time-slicing' discretization approach to the path integral – see Kleinert [6] for more details. For example, the singular $1/r$ potential occurring within the Coulomb/Hydrogen-like problem yields more and more singular behavior at higher orders in δt.

Using the result in eq. (16.1.6) we see that this stationary phase approximation tells us

$$\lim_{x\to+\infty}\int_a^b \exp(ix\varphi(t))\mathrm{d}t \sim \exp\left[ix\varphi(t_0)+i\frac{\pi}{4}\mathrm{sgn}[\varphi''(t_0)]\right]\sqrt{\frac{2\pi}{x|\varphi''(t_0)|}}, \tag{16.2.16}$$

[15]One of the conceptual advantages of using the path integral in eq. (16.0.1) to discuss the quantum mechanical transition amplitude is the ease in which we may define the classical limit. A physical process is (semi-)classical when we may associate with it position $\vec{q}$ and momentum $\vec{p}$, such that the exponent in eq. (16.0.1) has magnitude much greater than unity, in units where $\hbar \equiv 1$:

$$\int_{t'}^{t}\left(\vec{p}\cdot\dot{\vec{q}}-H(\vec{q},\vec{p})\right)\mathrm{d}s \gg 1. \tag{16.2.17}$$

When this criteria is filled, we may employ the stationary phase approximation to assert that the path integral is dominated by the stationary point, in the following sense. Let us consider

$$\vec{x} = \vec{Z}+\delta\vec{Z}, \tag{16.2.18}$$

$$\vec{p} = \vec{\Pi}+\delta\vec{\Pi} \tag{16.2.19}$$

where $\delta\vec{Z}$ and $\delta\vec{\Pi}$ are to be considered small perturbations relative to $\vec{Z}$ and $\vec{\Pi}$ respectively. Then,

$$\begin{aligned}\int_{t'}^{t}\left(\vec{p}\cdot\dot{\vec{q}}-H(\vec{q},\vec{p})\right)\mathrm{d}s = \int_{t'}^{t}\Bigg\{&\left(\vec{\Pi}\cdot\dot{\vec{Z}}-H(\vec{Z},\vec{\Pi})\right) \\ &+\delta\vec{\Pi}\cdot\left(\dot{\vec{Z}}-\frac{\partial H}{\partial\vec{\Pi}}\right)-\delta\vec{Z}\cdot\left(\dot{\vec{\Pi}}+\frac{\partial H}{\partial\vec{Z}}\right)+\mathcal{O}\left(\delta\vec{Z}^2,\delta\vec{\Pi}^2,\delta\vec{Z}\delta\vec{\Pi}\right)\Bigg\}\mathrm{d}s+\left[\delta\vec{Z}\cdot\vec{\Pi}\right]_{s=t'}^{s=t}.\end{aligned} \tag{16.2.20}$$

We should view this step as the infinite dimensional version of the 1D one in eq. (16.2.14). Note that the last term is actually zero because of the boundary condition implied by the path integral in eq. (16.0.1), that $\vec{Z}(s=t)=\vec{x}$ and $\vec{Z}(s=t')=\vec{x}'$ – i.e., $\vec{Z}$ is fixed at the end points, and thus $\delta\vec{Z}$ vanishes there. At this point, we make the key observation: the stationary point occurs when the first order terms proportional to $\delta\vec{\Pi}$ and $\delta\vec{Z}$ vanish. These yield the classical Hamilton's equations:

$$\dot{\vec{Z}} = \frac{\partial H}{\partial\vec{\Pi}} \qquad \text{and} \qquad \dot{\vec{\Pi}} = -\frac{\partial H}{\partial\vec{Z}}. \tag{16.2.21}$$

Just as the dominant contribution to the integral in eq. (16.2.14) arises from the neighborhood where $\varphi'(t_0)=0$, we see that the quantum mechanical amplitude for a particle to propagate from $\vec{x}'$ to $\vec{x}$ is dominated by the classical solution – i.e., obeying Hamilton's equations – subject to the boundary conditions $\vec{Z}(t)=\vec{x}$ and $\vec{Z}(t')=\vec{x}'$.

[15]If there is no such $t_0\in[a,b]$ such that $\varphi'(t_0)=0$, then $f(x\to+\infty)\sim 1/x$; i.e., the integral will decay more quickly than the case where a stationary point exists.

Quadratic-in-momentum & Lagrangian formulation The situation where H takes the form in eq. (16.2.4) occurs frequently. If it holds, we may in fact 'complete-the-square' and obtain the Lagrangian formulation of the path integral

$$\left\langle \vec{x} \left| e^{-iH(t-t')} \right| \vec{x}' \right\rangle = \mathcal{N} \int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q} \exp\left[i \int_{t'}^{t} \mathrm{d}s L\left(\vec{q}, \dot{\vec{q}}\right) \right], \tag{16.2.22}$$

$$L\left(\vec{q}, \dot{\vec{q}}\right) = \vec{p}(\dot{\vec{q}}) \cdot \dot{\vec{q}} - H\left(\vec{q}, \dot{\vec{q}}\right). \tag{16.2.23}$$

The first step is to recognize, if the Hamilton H does take the form in eq. (16.2.4) (this may involve setting the mass to unity), then the exponential involving $\vec{k}_i$ in eq. (16.2.9) can be written as

$$\exp\left(i \left\{ \vec{k}_i \cdot \frac{\vec{q}_{i+1} - \vec{q}_i}{\delta t_i} - \frac{\vec{k}_i^2}{2} - V(\vec{q}_{i+1}) \right\} \delta t_i \right) \tag{16.2.24}$$

$$= \exp\left(i \left\{ -\frac{1}{2} \left(\vec{k}_i - \frac{\vec{q}_{i+1} - \vec{q}_i}{\delta t_i} \right)^2 + \frac{(\vec{q}_{i+1} - \vec{q}_i)^2}{2\delta t_i^2} - V(\vec{q}_{i+1}) \right\} \delta t_i \right). \tag{16.2.25}$$

Integrating over $\vec{k}_i$ using eq. (16.1.6), and recognizing $(\vec{q}_{i+1} - \vec{q}_i)/\delta t_i$ as the finite difference approximation of the velocity $\dot{\vec{q}}(t_i)$, we see that eq. (16.2.9) now reads

$$\left\langle \vec{x} \left| e^{-iH(t-t')} \right| \vec{x}' \right\rangle = \lim_{N\to\infty} \int_{\mathbb{R}^D} \mathrm{d}^D \vec{q}_N \ldots \mathrm{d}^D \vec{q}_2 \prod_{i=1}^{N} \left(\frac{e^{-i\frac{\pi D}{4}}}{(2\pi\delta t_i)^{D/2}} \exp\left(i \left\{ \frac{1}{2} \dot{\vec{q}}_i(t_i)^2 - \vec{V}(\vec{q}_{i+1}) \right\} \delta t_i \right) \right);$$

$$\dot{\vec{q}}_i(t_i) \equiv \frac{\vec{q}_{i+1} - \vec{q}_i}{\delta t_i}, \qquad \vec{q}_1 \equiv \vec{x}', \qquad \text{and} \qquad \vec{q}_{N+1} \equiv \vec{x}. \tag{16.2.26}$$

(The square root is the positive one.) The shorthand for this expression is eq. (16.2.22).

Problem 16.3. Free Particle Path Integral Employ the result in eq. (16.2.26) to evaluate the path integral for the free particle, where $V = 0$. In other words, recover the result in eq. (16.1.9). Hint: You may need to re-arrange the exponents; start integrating from $\vec{q}_2$, then $\vec{q}_3$, etc. Also remember all the $\delta t_i \equiv \delta t$ are the same. □

Schrödinger's Equation We may shift the final time t by an infinitesimal $\mathrm{d}t$, and employ the result in eq. (16.2.26) by treating the final time interval as $\delta t_{N+1} \equiv \mathrm{d}t$.

$$\begin{aligned}
&\left\langle \vec{x} \left| e^{-iH(t+\mathrm{d}t-t')} \right| \vec{x}' \right\rangle \\
&= e^{-i\frac{\pi}{4}D} \sqrt{\frac{1}{2\pi \mathrm{d}t}}^D \int_{\mathbb{R}^D} \mathrm{d}^D \vec{q}_{N+1} \exp\left(i \left\{ \frac{(\vec{x} - \vec{q}_{N+1})^2}{2\mathrm{d}t} - V(\vec{x})\mathrm{d}t \right\} \right) \left\langle \vec{q}_{N+1} \left| e^{-iH(t-t')} \right| \vec{x}' \right\rangle \\
&= e^{-i\frac{\pi}{4}D} \sqrt{\frac{1}{2\pi \mathrm{d}t}}^D \int_{\mathbb{R}^D} \mathrm{d}^D \vec{q}' \exp\left(i \frac{\vec{q}'^2}{2\mathrm{d}t} \right) \left(1 - iV(\vec{x})\mathrm{d}t + \mathcal{O}(\mathrm{d}t^2) \right) \left\langle \vec{q}' + \vec{x} \left| e^{-iH(t-t')} \right| \vec{x}' \right\rangle \\
&= e^{-i\frac{\pi}{4}D} \sqrt{\frac{1}{\pi}}^D \int_{\mathbb{R}^D} \mathrm{d}^D \vec{q}' \exp\left(i\vec{q}'^2 \right) \left(1 - iV(\vec{x})\mathrm{d}t + \mathcal{O}(\mathrm{d}t^2) \right) \left\langle \sqrt{2\mathrm{d}t}\vec{q}' + \vec{x} \left| e^{-iH(t-t')} \right| \vec{x}' \right\rangle
\end{aligned}$$

$$
\begin{aligned}
&= e^{-i\frac{\pi}{4}D}\sqrt{\frac{1}{\pi}}^{D}\int_{\mathbb{R}^D}\mathrm{d}^D\vec{q}'\exp\left(-(-i)\vec{q}'^2\right)\left(1-iV(\vec{x})\mathrm{d}t+\mathcal{O}(\mathrm{d}t^2)\right)\\
&\quad\times\left(1+\sqrt{2\mathrm{d}t}\vec{q}'\cdot\vec{\nabla}_{\vec{x}}+\frac{1}{2}(2\mathrm{d}t)q'^{l_1}q'^{l_2}\partial_{l_1}\partial_{l_2}+\mathcal{O}(\mathrm{d}t^{3/2})\right)\left\langle\vec{x}\left|e^{-iH(t-t')}\right|\vec{x}'\right\rangle\\
&= e^{-i\frac{\pi}{4}D}\sqrt{\frac{1}{\pi}}^{D}\int_{\mathbb{R}^D}\mathrm{d}^D\vec{q}'\exp\left(-(-i)\vec{q}'^2\right)\left(1+\sqrt{2\mathrm{d}t}\vec{q}'\cdot\vec{\nabla}_{\vec{x}}+(\mathrm{d}t)q'^{l_1}q'^{l_2}\partial_{l_1}\partial_{l_2}-iV(\vec{x})\mathrm{d}t+\mathcal{O}(\mathrm{d}t^{3/2})\right)\\
&\qquad\qquad\times\left\langle\vec{x}\left|e^{-iH(t-t')}\right|\vec{x}'\right\rangle. \qquad (16.2.27)
\end{aligned}
$$

We have

$$\int_{\mathbb{R}^D}\mathrm{d}^D\vec{q}'\exp\left(i\vec{q}'^2\right)=\sqrt{\pi}^D e^{+i\frac{\pi D}{4}}. \qquad (16.2.28)$$

Additionally, because $e^{i\vec{q}'^2}\vec{q}'$ is odd in $\vec{q}'$,

$$\int_{\mathbb{R}^D}\mathrm{d}^D\vec{q}'\exp\left(i\vec{q}'^2\right)\vec{q}'=0; \qquad (16.2.29)$$

whereas

$$\int_{\mathbb{R}^D}\mathrm{d}^D\vec{q}'\exp\left(i\vec{q}'^2\right)q'^a q'^b=A\delta^{ab}; \qquad (16.2.30)$$

where A can be obtained by contracting both sides with respect to δ_{ab}.

$$\int_{\mathbb{R}^D}\mathrm{d}^D\vec{q}'\exp\left(i\vec{q}'^2\right)\vec{q}'^2=A\cdot D \qquad (16.2.31)$$

$$-i\partial_\lambda\int_{\mathbb{R}^D}\mathrm{d}^D\vec{q}'\exp\left(i\lambda\vec{q}'^2\right)\Big|_{\lambda=1}=-i\partial_\lambda\sqrt{\frac{\pi i}{\lambda}}^D\Big|_{\lambda=1}=D\cdot A \qquad (16.2.32)$$

Therefore

$$\int_{\mathbb{R}^D}\mathrm{d}^D\vec{q}'\exp\left(i\vec{q}'^2\right)q'^a q'^b=-\frac{i}{D}\left(-\frac{D}{2}\right)\sqrt{\pi i}^D\delta^{ab}=\frac{i}{2}\sqrt{\pi i}^D\delta^{ab}. \qquad (16.2.33)$$

Altogether, we now have

$$
\begin{aligned}
&\left\langle\vec{x}\left|e^{-iH(t+\mathrm{d}t-t')}\right|\vec{x}'\right\rangle=\left\langle\vec{x}\left|e^{-iH(t-t')}\right|\vec{x}'\right\rangle+\mathrm{d}t\partial_t\left\langle\vec{x}\left|e^{-iH(t-t')}\right|\vec{x}'\right\rangle+\mathcal{O}(\mathrm{d}t^2)\\
&=\left(1+i\mathrm{d}t\left\{\frac{1}{2}\vec{\nabla}^2_{\vec{x}}-V(\vec{x})\right\}+\mathcal{O}(\mathrm{d}t^{3/2})\right)\left\langle\vec{x}\left|e^{-iH(t-t')}\right|\vec{x}'\right\rangle. \qquad (16.2.34)
\end{aligned}
$$

Equating the order $\mathrm{d}t$ terms on both sides, we obtain Schrödinger's equation:

$$i\partial_t\left\langle\vec{x}\left|e^{-iH(t-t')}\right|\vec{x}'\right\rangle=\left(-\frac{1}{2}\vec{\nabla}^2_{\vec{x}}+V(\vec{x})\right)\left\langle\vec{x}\left|e^{-iH(t-t')}\right|\vec{x}'\right\rangle. \qquad (16.2.35)$$

In the other words, the time-sliced definition of the path integral obeys the Schrödinger's equation.

Heisenberg Picture Within the Heisenberg picture, recall that the position operator $\vec{X}_{\rm H}(t)$ is time-dependent (unless it commutes with the Hamiltonian). Therefore, so are its eigenkets. According to eq. (4.0.23),

$$|\vec{x},t\rangle_{\rm H} = U(t,t_0)^\dagger\,|\vec{x}\rangle\,. \tag{16.2.36}$$

We see that the path integral in eq. (16.0.1) can be expressed as

$${}_{\rm H}\,\langle\vec{x},t|\,\vec{x}',t'\rangle_{\rm H} = \int_{\vec{x}'}^{\vec{x}}\mathcal{D}\vec{q}\int\mathcal{D}\vec{p}\exp\left[i\int_{t'}^{t}\Big(\vec{p}\cdot\dot{\vec{q}}-H(\vec{q},\vec{p})\Big)\,\mathrm{d}s\right] \tag{16.2.37}$$

because

$$\begin{aligned}{}_{\rm H}\,\langle\vec{x},t|\,\vec{x}',t'\rangle_{\rm H} &= \left\langle\vec{x}\,\middle|U(t,t_0)U(t',t_0)^\dagger\middle|\,\vec{x}'\right\rangle &(16.2.38)\\ &= \langle\vec{x}\,|U(t,t_0)U(t_0,t')|\,\vec{x}'\rangle = \langle\vec{x}\,|U(t,t')|\,\vec{x}'\rangle\,. &(16.2.39)\end{aligned}$$

We have used the facts (cf. equations (3.0.11) and (3.0.12)) that

$$U(t_1,t_2)^\dagger = U(t_2,t_1) \tag{16.2.40}$$

and

$$U(t_1,t_2)U(t_2,t_3) = U(t_1,t_3). \tag{16.2.41}$$

Problem 16.4. What is

$$\int\mathrm{d}^D\vec{z}\int_{\vec{z}}^{\vec{x}}\mathcal{D}\vec{q}\exp\left[i\int_s^t\left(\frac{1}{2}\dot{\vec{q}}^2-V(\vec{q})\right)\mathrm{d}s\right]\int_{\vec{x}'}^{\vec{z}}\mathcal{D}\vec{q}'\exp\left[i\int_{t'}^{s}\left(\frac{1}{2}\dot{\vec{q}}'^2-V(\vec{q}')\right)\right]? \tag{16.2.42}$$

□

16.2.1 General Properties

Energy Eigenstates If we can perform the path integral exactly, this amounts to solving for the energy eigenfunctions, as can be seen by inserting the completeness relation $\sum_n |E_n\rangle\langle E_n| = \mathbb{I}$:

$$\begin{aligned}{}_{\rm H}\,\langle\vec{x},t|\,\vec{x}',t'\rangle_{\rm H} &= \langle\vec{x}\,|\exp[-iH(t-t')]|\,\vec{x}'\rangle &(16.2.43)\\ &= \sum_n\langle\vec{x}|\,E_n\rangle\,\langle E_n|\,\vec{x}'\rangle\,e^{-iE_n(t-t')} &(16.2.44)\\ H\,|E_n\rangle &= E_n\,|E_n\rangle\,. &(16.2.45)\end{aligned}$$

Partition Function If we require that the particle start and end at the same point $\vec{x} = \vec{x}' \equiv \vec{z}$, and then integrate over all space, we obtain the one-particle partition function:

$$\begin{aligned}\int\mathrm{d}^D\vec{z}\,{}_{\rm H}\,\langle\vec{z},t|\,\vec{z},t'\rangle_{\rm H} &= \sum_n\int\mathrm{d}^D\vec{z}\,\langle E_n|\,\vec{z}\rangle\,\langle\vec{z}|\,E_n\rangle\,e^{-iE_n(t-t')}\\ &= \sum_n e^{-iE_n(t-t')}. &(16.2.46)\end{aligned}$$

Green's function and Determinants Assume for the moment that $\mu > 0$, then consider

$$\int_0^\infty \mathrm{d}\tau e^{-\mu\tau} \left\langle \vec{x} \left| \exp[-iH\tau] \right| \vec{x}' \right\rangle = \sum_n \left\langle \vec{x} \right| E_n \rangle \left\langle E_n \right| \vec{x}' \rangle \left(\frac{e^{-iE_n\tau-\mu\tau}}{-iE_n - \mu} \right)_{\tau=0}^{\tau=\infty} \tag{16.2.47}$$

$$= \sum_n \frac{\left\langle \vec{x} \right| E_n \rangle \left\langle E_n \right| \vec{x}' \rangle}{\mu + iE_n} \tag{16.2.48}$$

We should be able to analytic continue the μ from real to "almost" purely imaginary $\mu \to i(\mu + i0^+)$, the 0^+ ensuring convergence of the integral. Then we have

$$G_{\mathrm{F}}[\vec{x}, \vec{x}'; \mu] \equiv i \int_0^\infty \mathrm{d}\tau e^{i(\mu+i0^+)\tau} \left\langle \vec{x} \left| \exp[-iH\tau] \right| \vec{x}' \right\rangle \tag{16.2.49}$$

$$= \sum_n \frac{\left\langle \vec{x} \right| E_n \rangle \left\langle E_n \right| \vec{x}' \rangle}{E_n - \mu - i0^+} = \left\langle \vec{x} \left| \frac{1}{H - \mu - i0^+} \right| \vec{x}' \right\rangle. \tag{16.2.50}$$

Notice, when viewed as a complex function of μ, this object has simple poles at the energy eigenvalues $\mu = E_n - i0^+$. Furthermore, if H is the Hamiltonian in the position rep, we then have the Green's function of the operator $H - \mu$:

$$(H_- \mu)\, G_{\mathrm{F}}[\vec{x}, \vec{y}; \mu] = \sum_n \left\langle \vec{x} \right| E_n \rangle \left\langle E_n \right| \vec{x}' \rangle \tag{16.2.51}$$

$$= \delta^D[\vec{x} - \vec{x}']. \tag{16.2.52}$$

Note that $(E_n - \omega)/(E_n - \omega - i0^+) = (E_n - \omega)/(E_n - \omega) + i\pi\delta[E_n - \omega](E_n - \omega) = 1$, because $z\delta(z) = 0$. In addition, if we trace over the positions and recall that the states $|E_n\rangle$ are of unit norm,

$$\int \mathrm{d}^D x G_{\mathrm{F}}[\vec{x}, \vec{x}; \mu] = \sum_n \frac{1}{E_n - \mu - i0^+} \equiv \mathrm{Tr}\left[\frac{1}{H - \mu} \right]. \tag{16.2.53}$$

Operator Insertions If we 'insert' an operator $O_{\mathrm{H}}(s)$ inside the transition amplitude ${}_{\mathrm{H}}\left\langle \vec{x}, t \right| \vec{x}', t' \rangle_{\mathrm{H}}$, where $t > s > t'$, let us show that – provided O is diagonal in the position representation, namely

$${}_{\mathrm{H}}\left\langle \vec{z}, s \left| O_{\mathrm{H}}(\vec{X}; s) \right| \vec{z}', s \right\rangle_{\mathrm{H}} = O\left(\vec{z}; s\right) \delta^{(D)}\left(\vec{z} - \vec{z}'\right), \tag{16.2.54}$$

where the O on the right hand side takes the same form as that on the left except the position operator $\vec{X}$ has been replaced with $\vec{z}$ (or $\vec{z}'$) – we have:

$${}_{\mathrm{H}}\left\langle \vec{x}, t \left| O_{\mathrm{H}}(s) \right| \vec{x}', t' \right\rangle_{\mathrm{H}} = \int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q} \int \mathcal{D}\vec{p}\, O(s) \exp\left(i \int_{t'}^{t} \left\{ \vec{p} \cdot \dot{\vec{q}} - H[\vec{p}, \vec{q}] \right\} \mathrm{d}\tau \right), \tag{16.2.55}$$

$$t > s > t'. \tag{16.2.56}$$

The analog of this object in Quantum Field Theory occurs frequently. Let us insert the Heisenberg-picture version of the completeness relation, i.e., eq. (4.0.25), on the left and right of O_{H}.

$${}_{\mathrm{H}}\left\langle \vec{x}, t \left| O_{\mathrm{H}}(s) \right| \vec{x}', t' \right\rangle_{\mathrm{H}}$$

$$= \int_{\mathbb{R}^D} \mathrm{d}^D\vec{z} \int_{\mathbb{R}^D} \mathrm{d}^D\vec{z}' \; {}_{\mathrm{H}}\langle \vec{x}, t | \, \vec{z}, s\rangle_{\mathrm{H}} \; {}_{\mathrm{H}}\langle \vec{z}, s \, | O_{\mathrm{H}}(s) | \, \vec{z}', s\rangle_{\mathrm{H}} \; {}_{\mathrm{H}}\langle \vec{z}', s | \, \vec{x}', t'\rangle_{\mathrm{H}} \tag{16.2.57}$$

$$= \int_{\mathbb{R}^D} \mathrm{d}^D\vec{z} \int_{\mathbb{R}^D} \mathrm{d}^D\vec{z}' \; {}_{\mathrm{H}}\langle \vec{x}, t | \, \vec{z}, s\rangle_{\mathrm{H}} \, O_{\mathrm{H}}(\vec{z}; s)\delta^{(D)}(\vec{z} - \vec{z}') \; {}_{\mathrm{H}}\langle \vec{z}', s | \, \vec{x}', t'\rangle_{\mathrm{H}} \tag{16.2.58}$$

$$= \int_{\mathbb{R}^D} \mathrm{d}^D\vec{z} \; {}_{\mathrm{H}}\langle \vec{x}, t | \, \vec{z}, s\rangle_{\mathrm{H}} \, O_{\mathrm{H}}(\vec{z}; s) \; {}_{\mathrm{H}}\langle \vec{z}, s | \, \vec{x}', t'\rangle_{\mathrm{H}} \, . \tag{16.2.59}$$

If we now exploit eq. (16.2.9),

$$\begin{aligned}
&{}_{\mathrm{H}}\langle \vec{x}, t \, | O_{\mathrm{H}}(s) | \, \vec{x}', t'\rangle_{\mathrm{H}} \qquad (16.2.60)\\
&= \lim_{N\to\infty} \int_{\mathbb{R}^D} \mathrm{d}^D\vec{q}_N \ldots \mathrm{d}^D\vec{q}_2 \int_{\mathbb{R}^D} \frac{\mathrm{d}^D\vec{k}_N}{(2\pi)^D} \cdots \frac{\mathrm{d}^D\vec{k}_1}{(2\pi)^D}\\
&\times \lim_{N'\to\infty} \int_{\mathbb{R}^D} \mathrm{d}^D\vec{q}'_{N'} \ldots \mathrm{d}^D\vec{q}'_2 \int_{\mathbb{R}^D} \frac{\mathrm{d}^D\vec{k}'_{N'}}{(2\pi)^D} \cdots \frac{\mathrm{d}^D\vec{k}'_1}{(2\pi)^D}\\
&\times \int_{\mathbb{R}^D} \mathrm{d}^D\vec{z} \, O(\vec{z}; s)\\
&\times e^{i\vec{k}_N\cdot(\vec{x}-\vec{q}_N) - iH(\vec{x},\vec{k}_N)\delta t_N} e^{i\vec{k}_{N-1}\cdot(\vec{q}_N-\vec{q}_{N-1}) - iH(\vec{q}_N,\vec{k}_{N-1})\delta t_{N-1}}\\
&\times e^{i\vec{k}_{N-2}\cdot(\vec{q}_{N-1}-\vec{q}_{N-2}) - iH(\vec{q}_{N-1},\vec{k}_{N-2})\delta t_{N-2}} \cdots e^{i\vec{k}_1\cdot(\vec{q}_2-\vec{z}) - iH(\vec{q}_2,\vec{k}_1)\delta t_1}\\
&\times e^{i\vec{k}'_{N'}\cdot(\vec{z}'-\vec{q}'_{N'}) - iH(\vec{z}',\vec{k}'_{N'})\delta t'_{N'}} e^{i\vec{k}'_{N'-1}\cdot(\vec{q}'_{N'}-\vec{q}'_{N'-1}) - iH(\vec{q}'_{N'},\vec{k}'_{N'-1})\delta t'_{N'-1}}\\
&\times e^{i\vec{k}'_{N'-2}\cdot(\vec{q}'_{N'-1}-\vec{q}'_{N'-2}) - iH(\vec{q}'_{N'-1},\vec{k}'_{N'-2})\delta t'_{N'-2}} \cdots e^{i\vec{k}'_1\cdot(\vec{q}'_2-\vec{x}') - iH(\vec{q}'_2,\vec{k}'_1)\delta t'_1}\\
&t - s \equiv \delta t_N + \cdots + \delta t_1, \qquad\qquad s - t' \equiv \delta t'_{N'} + \cdots + \delta t'_1.
\end{aligned}$$

If O were simply the identity, we'd recover eq. (16.2.9). But with O present this merely means we'd have to, at the s-time-slice, also integrate over it. That is, eq. (16.2.60) is the continuum limit of eq. (16.2.60).

Energy Eigenstates Expectation Values in Heisenberg Picture We may express the expectation value of some operator O with respect to an energy eigenket state in terms of path integrals. We will continue to assume eq. (16.2.54) holds; i.e., O is diagonal in the position representation. Specifically, keeping in mind eq. (16.2.55),

$$\langle E \, | O | \, E\rangle = \frac{\int_{\mathbb{R}^D} \mathrm{d}^D\vec{x} \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x}' \; \langle E | \, \vec{x}\rangle \; {}_{\mathrm{H}}\langle \vec{x}, t_1 \, | O_{\mathrm{H}}(t) | \, \vec{x}', t_2\rangle_{\mathrm{H}} \; \langle \vec{x}' | \, E\rangle}{{}_{\mathrm{H}}\langle E, t_1 | \, E, t_2\rangle_{\mathrm{H}}}, \tag{16.2.61}$$

$${}_{\mathrm{H}}\langle E, t_1 | \, E, t_2\rangle_{\mathrm{H}} = \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x} \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x}' \; \langle E | \, \vec{x}\rangle \; {}_{\mathrm{H}}\langle \vec{x}, t_1 | \, \vec{x}', t_2\rangle_{\mathrm{H}} \; \langle \vec{x}' | \, E\rangle \, ; \tag{16.2.62}$$

where $t_{1,2}$ are arbitrary (as long as they are not equal to t) and the energy eigen-functions $\langle \vec{x} | \, E\rangle$ are written in the Schrödinger picture. The situation in eq. (16.2.61) occurs frequently within QFT, particularly when $|E\rangle$ refers to the vacuum state.

Using eq. (4.0.28), we begin with the numerator on the right hand side of eq. (16.2.61).

$$\int_{\mathbb{R}^D} \mathrm{d}^D\vec{x} \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x}' \; \langle E | \, \vec{x}\rangle \; {}_{\mathrm{H}}\langle \vec{x}, t_1 \, | O_{\mathrm{H}}(t) | \, \vec{x}', t_2\rangle_{\mathrm{H}} \; \langle \vec{x}' | \, E\rangle \tag{16.2.63}$$

$$= \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x} \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x}' \; {}_{\mathrm{H}}\langle E, t_1 | \, \vec{x}, t_1\rangle \; {}_{\mathrm{H}}{}_{\mathrm{H}}\langle \vec{x}, t_1 \, | O_{\mathrm{H}}(t) | \, \vec{x}', t_2\rangle_{\mathrm{H}} \; {}_{\mathrm{H}}\langle \vec{x}', t_2 | \, E, t_2\rangle \; {}_{\mathrm{H}} \tag{16.2.64}$$

Next we employ the Heisenberg-picture completeness relation in eq. (4.0.25).

$$\int_{\mathbb{R}^D} \mathrm{d}^D\vec{x} \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x}' \, \langle E|\,\vec{x}\rangle \, {}_{\mathrm{H}}\langle \vec{x}, t_1\,|O_{\mathrm{H}}(t)|\,\vec{x}', t_2\rangle_{\mathrm{H}} \, \langle \vec{x}'|\,E\rangle = {}_{\mathrm{H}}\langle E, t_1\,|O_{\mathrm{H}}(t)|\,E, t_2\rangle \, {}_{\mathrm{H}} \tag{16.2.65}$$

Now, let us recall equations (4.0.9) and (4.0.23) to return to the Schrödinger picture.

$$\int_{\mathbb{R}^D} \mathrm{d}^D\vec{x} \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x}' \, \langle E|\,\vec{x}\rangle \, {}_{\mathrm{H}}\langle \vec{x}, t_1\,|O_{\mathrm{H}}(t)|\,\vec{x}', t_2\rangle_{\mathrm{H}} \, \langle \vec{x}'|\,E\rangle \tag{16.2.66}$$

$$= \langle E|\, e^{-iE(t_1-t_0)} e^{iE(t-t_0)} O e^{-iE(t-t_0)} e^{iE(t_2-t_0)}\,|E\rangle \tag{16.2.67}$$

$$= e^{-iE(t_1-t_2)}\,\langle E|\,O\,|E\rangle = \langle E|\, e^{-iE(t_1-t_0)} e^{iE(t_2-t_0)}\,|E\rangle\,\langle E|\,O\,|E\rangle \tag{16.2.68}$$

$$= {}_{\mathrm{H}}\langle E, t_1|\,E, t_2\rangle \, {}_{\mathrm{H}} \cdot \langle E|\,O\,|E\rangle\,. \tag{16.2.69}$$

Dividing both sides by ${}_{\mathrm{H}}\langle E, t_1|\,E, t_2\rangle\,{}_{\mathrm{H}}$, we arrive at eq. (16.2.61). Moreover, when we set $O = \mathbb{I}$ on both sides, we have also recover the representation in eq. (16.2.62).

> For time-independent H, the energy eigenstate expectation value of some operator O in the Schrödinger picture can be expressed as a ratio of path integrals integrated against the energy-eigenfunctions at the initial and final times – with O inserted in the numerator path integral.

Problem 16.5. Time-Ordered Products from Path Integrals Show that operator insertions within the path integral, namely

$$\int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q} \int \mathcal{D}\vec{p} \exp\left(i \int_{t'}^{t} \left\{ \vec{p}\cdot\dot{\vec{q}} - H[\vec{q},\vec{p}] \right\} \mathrm{d}s \right) A(s)B(s')C(s'')\ldots \tag{16.2.70}$$

$$= {}_{\mathrm{H}}\langle \vec{x}, t\,|\mathsf{T}\,\{A_{\mathrm{H}}(s)B_{\mathrm{H}}(s')C_{\mathrm{H}}(s'')\ldots\}|\,\vec{x}', t'\rangle_{\mathrm{H}}\,; \tag{16.2.71}$$

where on the right hand side A_{H}, B_{H}, C_{H}, ... are arbitrary Heisenberg-picture operators diagonal in the position representation; and A, B, C, ... on the left-hand-side correspond to their complex-number counterparts; and $t > (s, s', s'', \ldots) > t'$. Whereas, T means the operators within the curly brackets are arranged such that the ones with later times stand on the right. For instance, if $s_2 > s_1$, then

$$\mathsf{T}\,\{A_{\mathrm{H}}(s_1)B_{\mathrm{H}}(s_2)\} = B_{\mathrm{H}}(s_2)A_{\mathrm{H}}(s_1); \tag{16.2.72}$$

or, if $s'' > s > s'$, then

$$\mathsf{T}\,\{A_{\mathrm{H}}(s)B_{\mathrm{H}}(s')C_{\mathrm{H}}(s'')\} = C_{\mathrm{H}}(s'')A_{\mathrm{H}}(s)B_{\mathrm{H}}(s'). \tag{16.2.73}$$

Hint: Insert completeness relations using the position eigenkets in the Heisenberg-picture. Such "correlation functions" are central objects in QFT; for instance, through the Lehmann-Symanzik-Zimmermann reduction, one may obtain the quantum scattering amplitude of n particles. □

16.2.2 Free Particle

We have already worked out the free particle path integral, so let us simply summarize the various representations here. From equations (16.1.3) and (16.1.9):

$$\left\langle \vec{x} \left| \exp\left[-i\frac{\vec{p}^2}{2m}(t-t')\right] \right| \vec{x}' \right\rangle = \int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q} \int \mathcal{D}\vec{p} \exp\left[i \int_{t'}^{t} \left(\vec{p}\cdot\dot{\vec{q}} - \frac{\vec{p}^2}{2} \right) \mathrm{d}s \right] \tag{16.2.74}$$

$$= \mathcal{N} \int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q} \exp\left[i \int_{t'}^{t} \frac{m}{2}\dot{\vec{q}}^2 \mathrm{d}s \right] \tag{16.2.75}$$

$$= \int_{\mathbb{R}^D} \frac{\mathrm{d}^D\vec{k}}{(2\pi)^D} \exp\left[i\vec{k}\cdot(\vec{x}-\vec{x}') - i\frac{\vec{k}^2}{2m}(t-t') \right] \tag{16.2.76}$$

$$= \exp\left[\frac{im}{2(t-t')}(\vec{x}-\vec{x}')^2 \right] e^{-i\frac{\pi D}{4}\mathrm{sgn}[t-t']} \left(\frac{m}{2\pi|t-t'|} \right)^{\frac{D}{2}}. \tag{16.2.77}$$

16.2.3 Simple Harmonic Oscillator

In this section we are going to compute the path integral of the simple harmonic oscillator. Because the SHO Hamiltonian takes the form in eq. (16.2.4), with the potential being $V(\vec{q}) = (\omega^2/2)\vec{q}^2$, we may thus start with the Lagrangian formulation in eq. (16.2.22):

$$K_J[t,t';\vec{x},\vec{x}'] \equiv \int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q} \exp\left[iS\right]; \tag{16.2.78}$$

where

$$S \equiv \int_{t'}^{t} L\mathrm{d}s; \tag{16.2.79}$$

$$L \equiv \frac{1}{2}\left(\dot{\vec{q}}[s]^2 - \omega^2\vec{q}[s]^2 \right). \tag{16.2.80}$$

The strategy is as follows. Like the free particle case, we split the $\vec{q}$ into a classical $\vec{q}_c$ and fluctuating piece $\vec{\xi}$, so that

$$\vec{q} \equiv \vec{q}_c + \vec{\xi}, \tag{16.2.81}$$

$$\mathcal{D}\vec{q} = \mathcal{D}\vec{\xi}; \tag{16.2.82}$$

with the boundary conditions

$$\vec{q}_c[t'] = \vec{x}', \qquad \vec{q}_c[t] = \vec{x}, \qquad \vec{\xi}[t'] = \vec{\xi}[t] = \vec{0}. \tag{16.2.83}$$

The Lagrangian now transforms into

$$L = L_0 + \dot{\vec{q}}_c\cdot\dot{\vec{\xi}} - \omega^2\vec{q}_c\cdot\vec{\xi} + \frac{1}{2}\left(\dot{\vec{\xi}}^2 - \omega^2\vec{\xi}^2 \right), \tag{16.2.84}$$

$$L_0 \equiv \frac{1}{2}\left(\dot{\vec{q}}_c^2 - \omega^2\vec{q}_c^2 \right). \tag{16.2.85}$$

The action now reads

$$S = S_0 + \left[\vec{\xi}\cdot\dot{\vec{q}}_c\right]_{t'}^{t} + \int_{t'}^{t} \mathrm{d}s \Bigg\{ -\vec{\xi}\cdot\left(\left(\frac{\mathrm{d}^2}{\mathrm{d}t^2}+\omega^2\right)\vec{q}_c\right) + \frac{1}{2}\left(\dot{\vec{\xi}}^2 - \omega^2\vec{\xi}^2\right)\Bigg\},$$
$$S_0 \equiv \frac{1}{2}\int_{t'}^{t}\left(\dot{\vec{q}}_c^2 - \omega^2\vec{q}_c^2\right)\mathrm{d}s. \tag{16.2.86}$$

We may demand that

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}t^2}+\omega^2\right)\vec{q}_c = \vec{0}. \tag{16.2.87}$$

Problem 16.6. With the boundary conditions in eq. (16.2.83), verify that the solution to the classical trajectory is

$$\vec{q}_c[s] = \frac{\vec{x}\sin\left[\omega(s-t')\right] + \vec{x}'\sin\left[\omega(t-s)\right]}{\sin\left[\omega(t-t')\right]}; \tag{16.2.88}$$

whenever the time elapsed is not a half-period, namely

$$\omega(t-t') \neq \ell\pi \qquad \text{(for integer } \ell\text{)}. \tag{16.2.89}$$

Next, show that the action now reads

$$S = S_c + \int_{t'}^{t}\mathrm{d}s\left(\frac{1}{2}\dot{\vec{\xi}}^2 - \frac{\omega^2}{2}\vec{\xi}^2\right); \tag{16.2.90}$$

where the classical contribution to the action is

$$S_c[\vec{q}_c] = \frac{\omega}{2\sin\left[\omega(t-t')\right]}\left((\vec{x}^2+\vec{x}'^2)\cos\left[\omega(t-t')\right] - 2\vec{x}\cdot\vec{x}'\right). \tag{16.2.91}$$

□

Now, as long as $t-t'$ is not a half-period, eq. (16.2.89) is valid, our path integral now reads

$$K[t,t';\vec{x},\vec{x}'] = \exp\left[\frac{i\omega}{2\sin\left[\omega(t-t')\right]}\left((\vec{x}^2+\vec{x}'^2)\cos\left[\omega(t-t')\right] - 2\vec{x}\cdot\vec{x}'\right)\right]$$
$$\times \int_{\vec{0}}^{\vec{0}}\mathcal{D}\vec{\xi}\exp\left[i\int_{t'}^{t}\mathrm{d}s\left(\frac{1}{2}\dot{\vec{\xi}}^2 - \frac{\omega^2}{2}\vec{\xi}^2\right)\right]. \tag{16.2.92}$$

Mode Sums & Functional Determinants We may now decompose $\vec{\xi}$ into a superposition of the complete set of eigen-functions of $(\mathrm{d}/\mathrm{d}s)^2+\omega^2$, subject to the boundary condition in eq. (16.2.83). Specifically, we may define the inner product of $\vec{\xi}_{1,2}(s)$ to be

$$\left\langle\vec{\xi}_1\middle|\,\vec{\xi}_2\right\rangle \equiv \int_{t'}^{t}\vec{\xi}_1\cdot\vec{\xi}_2\mathrm{d}s, \tag{16.2.93}$$
$$\vec{\xi}_{1,2}(s=t') = \vec{0} = \vec{\xi}_{1,2}(s=t). \tag{16.2.94}$$

In particular, the differential operator $(\mathrm{d}/\mathrm{d}s)^2+\omega^2$ is Hermitian

$$\int_{t'}^{t}\left(\frac{\mathrm{d}^2}{\mathrm{d}s^2}+\omega^2\right)\vec{\xi}_1(s)\cdot\vec{\xi}_2\mathrm{d}s=\int_{t'}^{t}\vec{\xi}_1(s)\cdot\left(\frac{\mathrm{d}^2}{\mathrm{d}s^2}+\omega^2\right)\vec{\xi}_2\mathrm{d}s \tag{16.2.95}$$

because the boundary terms vanishes by eq. (16.2.93).

Moreover, the orthonormal eigenfunctions are

$$u_\ell[s]=\sqrt{\frac{2}{t-t'}}\sin\left[\frac{\ell\pi}{t-t'}(s-t')\right], \tag{16.2.96}$$

$$\int_{t'}^{t}u_m\cdot u_n\mathrm{d}s=\delta_{mn}, \tag{16.2.97}$$

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}s^2}+\omega^2\right)u_\ell=-\lambda_\ell u_\ell,\qquad\qquad \lambda_\ell\equiv\omega^2\left\{\ell^2\left(\frac{\pi}{\omega(t-t')}\right)^2-1\right\}. \tag{16.2.98}$$

Since the eigen-functions of $(\mathrm{d}/\mathrm{d}s)^2+\omega^2$ must be complete,

$$\vec{\xi}=\sum_{\ell=1}^{\infty}\vec{Z}_\ell u_\ell[s]. \tag{16.2.99}$$

Note that $u_\ell[t]=u_\ell[t']=0$; and

$$\tag{16.2.100}$$

Therefore,

$$\frac{1}{2}\int_{t'}^{t}\mathrm{d}s\left(\dot{\vec{\xi}}^2-\omega^2\vec{\xi}^2\right)=-\frac{1}{2}\sum_{m,n=1}^{\infty}\vec{Z}_m\cdot\vec{Z}_n\delta_{mn}\left(-\lambda_n\right)=\frac{1}{2}\sum_{n=1}^{\infty}\vec{Z}_n^2\lambda_n; \tag{16.2.101}$$

and

$$\exp\left[\frac{i}{2}\int_{t'}^{t}\left(\dot{\vec{\xi}}^2-\omega^2\vec{\xi}^2\right)\mathrm{d}s\right]=\prod_{\ell=1}^{+\infty}\exp\left[\frac{i}{2}\lambda_\ell\vec{Z}_\ell^2\right]. \tag{16.2.102}$$

We may now interpret, using eq. (16.2.98),

$$\begin{aligned}\int_{\vec{0}}^{\vec{0}}\mathcal{D}\vec{\xi}\exp\left[i\int_{t'}^{t}\mathrm{d}s\left(\frac{1}{2}\dot{\vec{\xi}}^2-\frac{\omega^2}{2}\vec{\xi}^2\right)\right]&=\mathcal{N}\prod_{\ell=1}^{+\infty}\int_{\mathbb{R}^D}\mathrm{d}^D\vec{Z}_\ell\exp\left[\frac{i}{2}\lambda_\ell\vec{Z}_\ell^2\right]\\&=\mathcal{N}'\prod_{\ell=1}^{+\infty}e^{\frac{iD\pi}{4}\mathrm{sgn}[\lambda_\ell]}\left|\omega^2-\left(\frac{\ell\pi}{t-t'}\right)^2\right|^{-\frac{D}{2}}\end{aligned} \tag{16.2.103}$$

Upon comparison with eq. (16.2.98), notice this $\vec{0}\to\vec{0}$ transition amplitude is proportional to the $-(D/2)$th power of the product of the eigenvalues of the SHO operator $(\mathrm{d}/\mathrm{d}s)^2+\omega^2$ subject to Dirichlet boundary conditions; this in turn is why the $\left\langle\vec{0}\left|U\right|\vec{0}\right\rangle$ is often dubbed a functional

determinant, since it is directly related to the determinant of the differential operator associated with the dynamics at hand.

$$\det\left(\frac{\mathrm{d}^2}{\mathrm{d}s^2}+\omega^2\right)\equiv\prod_{\ell=1}^{\infty}\left(\omega^2-\left(\frac{\ell\pi}{t-t'}\right)^2\right) \tag{16.2.104}$$

$$\int_{\vec{0}}^{\vec{0}}\mathcal{D}\vec{\xi}\exp\left[i\int_{t'}^{t}\mathrm{d}s\left(\frac{1}{2}\dot{\vec{\xi}}^2-\frac{\omega^2}{2}\vec{\xi}^2\right)\right]\propto\left\{\det\left(\frac{\mathrm{d}^2}{\mathrm{d}s^2}+\omega^2\right)\right\}^{-\frac{D}{2}}. \tag{16.2.105}$$

At this point, note that the pre-factors $\mathcal{N}$ and $\mathcal{N}'$ should not depend on ω, since it arises from the ambiguity of the integration measure $\mathcal{D}\vec{\xi}\to\prod_\ell \mathrm{d}^D\vec{Z}_\ell$. We proceed as follows.

$$\begin{aligned}\int_{\vec{0}}^{\vec{0}}\mathcal{D}\vec{\xi}\exp\left[i\int_{t'}^{t}\mathrm{d}s\left(\frac{1}{2}\dot{\vec{\xi}}^2-\frac{\omega^2}{2}\vec{\xi}^2\right)\right]&=\mathcal{N}'\prod_{\ell'=1}^{\infty}\left(\left|\frac{\ell'\pi}{t-t'}\right|^{-D}e^{\frac{iD\pi}{4}\mathrm{sgn}[\lambda_{\ell'}]}\right)\prod_{\ell=1}^{+\infty}\left|1-\left(\frac{\omega(t-t')}{\ell\pi}\right)^2\right|^{-\frac{D}{2}}\\&=\mathcal{N}_2[t-t']\left|\frac{\omega(t-t')}{\sin[\omega(t-t')]}\right|^{\frac{D}{2}},\\\mathcal{N}_2[t-t']&\equiv\mathcal{N}'\prod_{\ell'=1}^{\infty}\left(\left|\frac{\ell'\pi}{t-t'}\right|^{-D}e^{\frac{iD\pi}{4}\mathrm{sgn}[\lambda_{\ell'}]}\right).\end{aligned} \tag{16.2.106}$$

We have utilized

$$\frac{\sin z}{z}=\prod_{\ell=1}^{\infty}\left(1-\frac{z^2}{(\ell\pi)^2}\right). \tag{16.2.107}$$

Let us observe that the sign of the eigenvalues in eq. (16.2.98),

$$\lambda_\ell\equiv\omega^2\left(\frac{\pi}{\omega(t-t')}\right)^2\left\{\ell^2-\left(\frac{\omega(t-t')}{\pi}\right)^2\right\}, \tag{16.2.108}$$

is controlled by the difference between the integer ℓ and $\omega(t-t')/\pi$ (for $t-t'>0$). (Note that, within classical dynamics, a full period $t-t'\equiv T$ of motion is determined by the equation $\omega T=2\pi$; so $t-t'=\pi/\omega$ is a half period.) When $0<\omega(t-t')/\pi<1$, i.e., within the first half-period, all the eigenvalues labeled by $\{\lambda_\ell|\ell=1,2,3,\dots\}$ are positive and

$$\mathcal{N}_2[t-t']\equiv\mathcal{N}'\prod_{\ell'=1}^{\infty}\left(\left|\frac{\ell'\pi}{t-t'}\right|^{-D}e^{\frac{iD\pi}{4}}\right). \tag{16.2.109}$$

It is important to note that $\mathcal{N}_2$ depends on time but not on ω. This means we may determine its form by taking the $\omega\to 0$ limit,[16] since it needs to recover the free particle case

$$\left\langle\vec{x}\left|e^{-i(t-t')\vec{p}^2/2}\right|\vec{x}'\right\rangle=\int_{\mathbb{R}^D}\frac{\mathrm{d}^D\vec{k}}{(2\pi)^D}e^{i\vec{k}\cdot(\vec{x}-\vec{x}')}e^{-i(t-t')\vec{k}^2/2} \tag{16.2.110}$$

[16] This is also why it is important to assume $0<\omega(t-t')<\pi$ because, as we shall see, the other time intervals $\ell\pi<\omega(t-t')<(\ell+1)\pi$ (for $\ell=1,2,3,\dots$) are not continuously connected to the free particle $\omega=0$ case.

Denoting $\vec{x}-\vec{x}'\equiv\vec{R}$ and $t-t'\equiv T$, we first complete the square.

$$-\frac{T}{2}\left(\left(\vec{k}-\frac{\vec{R}}{T}\right)^2-\frac{R^2}{T^2}\right)=-\frac{T}{2}\left(\vec{k}^2-\frac{2}{T}\vec{k}\cdot\vec{R}\right) \tag{16.2.111}$$

For $T>0$,

$$\begin{aligned}\left\langle\vec{x}\left|e^{-i(t-t')\vec{p}^2/2}\right|\vec{x}'\right\rangle &= e^{\frac{i}{2}\frac{R^2}{T}}\int_{\mathbb{R}^D}\frac{\mathrm{d}^D\vec{k}}{(2\pi)^D}e^{-i(t-t')\vec{k}^2/2}\\ &= e^{\frac{i}{2}\frac{R^2}{T}}\left(\frac{e^{-i\frac{\pi}{4}}}{2\pi}\sqrt{\frac{2\pi}{|t-t'|}}\right)^D. \end{aligned}\tag{16.2.112}$$

When $\vec{x}=\vec{x}'=\vec{0}$,

$$\left\langle\vec{0}\left|e^{-i(t-t')\vec{p}^2/2}\right|\vec{0}\right\rangle=\left(\frac{e^{-i\frac{\pi}{4}}}{\sqrt{2\pi|t-t'|}}\right)^D. \tag{16.2.113}$$

and therefore, for $0<\omega(t-t')<\pi$, we have the result

$$\int_{\vec{0}}^{\vec{0}}\mathcal{D}\vec{\xi}\exp\left[i\int_{t'}^{t}\mathrm{d}s\left(\frac{1}{2}\dot{\vec{\xi}}^2-\frac{\omega^2}{2}\vec{\xi}^2\right)\right]=e^{-iD\frac{\pi}{4}}\left|\frac{1}{2\pi(t-t')}\right|^{\frac{D}{2}}\left|\frac{\omega(t-t')}{\sin[\omega(t-t')]}\right|^{\frac{D}{2}} \tag{16.2.114}$$

$$=e^{-iD\frac{\pi}{4}}\left|\frac{\omega}{2\pi\sin[\omega(t-t')]}\right|^{\frac{D}{2}}. \tag{16.2.115}$$

When the elapsed time $t-t'$ lies within the second half-period, $1<\omega(t-t')/\pi<2$, then the first eigenvalue λ_1 in eq. (16.2.108) becomes negative whereas the rest of the $\lambda_{\ell>1}$ remain positive. The overall amplitude $\mathcal{N}_2$ multiplying the SHO path integral in eq. (16.2.106) then reads

$$\mathcal{N}_2[t-t']=\mathcal{N}'\cdot\left(\left|\frac{\pi}{t-t'}\right|^{-D}e^{-\frac{iD\pi}{4}}\right)\cdot\prod_{\ell'=2}^{\infty}\left(\left|\frac{\ell'\pi}{t-t'}\right|^{-D}e^{\frac{iD\pi}{4}}\right) \tag{16.2.116}$$

$$=\mathcal{N}'\prod_{\ell'=1}^{\infty}\left(\left|\frac{\ell'\pi}{t-t'}\right|^{-D}e^{\frac{iD\pi}{4}}\right)e^{-i\frac{\pi}{2}D}. \tag{16.2.117}$$

The phase in the first factor has become $e^{-i(\pi D)/4}=e^{+i(\pi D)/4}e^{-i(\pi D)/2}$; and since $\mathcal{N}_2$ multiplies the path integral, we see the quantum mechanical transition amplitude would therefore jump by a phase $e^{-i(\pi D/2)}$ when the time elapsed $t-t'$ proceeds from the first to second half-period. In the third half-period, $2<\omega(t-t')/\pi<3$, eq. (16.2.108) indicates both λ_1 and λ_2 are now negative and

$$\mathcal{N}_2[t-t']=\mathcal{N}'\prod_{\ell'=1}^{\infty}\left(\left|\frac{\ell'\pi}{t-t'}\right|^{-D}e^{\frac{iD\pi}{4}}\right)e^{-i2\cdot\frac{\pi}{2}D}. \tag{16.2.118}$$

More generally, as $t-t'$ transitions from the ℓth half-period to the $(\ell+1)$th one, the $\lambda_{\ell+1}$ eigenvalue will flip sign from $+$ to $-$, which in turn will cause a jump in the phase multiplying the path integral by $e^{-i(\pi D/2)}$. To sum, when

$$0<\ell<\frac{\omega(t-t')}{\pi}<\ell+1, \tag{16.2.119}$$

the $\vec{0}$ to $\vec{0}$ path integral is

$$\int_{\vec{0}}^{\vec{0}}\mathcal{D}\vec{\xi}\exp\left[i\int_{t'}^{t}\mathrm{d}s\left(\frac{1}{2}\dot{\vec{\xi}}^2-\frac{\omega^2}{2}\vec{\xi}^2\right)\right]=e^{-i\ell\frac{\pi D}{2}}e^{-iD\frac{\pi}{4}}\left|\frac{\omega}{2\pi\sin[\omega(t-t')]}\right|^{\frac{D}{2}}; \tag{16.2.120}$$

and eq. (16.2.92) becomes

$$\begin{aligned}K[t,t';\vec{x},\vec{x}']=&\exp\left[\frac{i\omega}{2\sin\left[\omega(t-t')\right]}\left((\vec{x}^2+\vec{x}'^2)\cos\left[\omega(t-t')\right]-2\vec{x}\cdot\vec{x}'\right)\right]\\&\times e^{-i\ell\frac{\pi D}{2}}e^{-iD\frac{\pi}{4}}\left|\frac{\omega}{2\pi\sin[\omega(t-t')]}\right|^{\frac{D}{2}}.\end{aligned} \tag{16.2.121}$$

Problem 16.7. SHO Path Integral & Classical Dynamics Recalling eq. (16.2.91), we may write eq. (16.2.121) as

$$\int_{\vec{x}'}^{\vec{x}}\mathcal{D}\vec{q}\exp\left[\frac{i}{2}\int_{t'}^{t}\left(\dot{\vec{q}}^2-\omega^2\vec{q}^2\right)\mathrm{d}s\right]=e^{-i\ell\frac{\pi D}{2}}e^{-iD\frac{\pi}{4}}\left|\frac{\omega}{2\pi\sin[\omega(t-t')]}\right|^{\frac{D}{2}}e^{iS_c[\vec{q}_c]}, \tag{16.2.122}$$

$$\ell<\frac{\omega(t-t')}{\pi}<\ell+1. \tag{16.2.123}$$

Show that, up to overall multiplicative phase factors, this result may be re-expressed as

$${}_{\mathrm{H}}\left\langle\vec{x},t\right|\left.\vec{x}',t'\right\rangle_{\mathrm{H}}=\int_{\vec{x}'}^{\vec{x}}\mathcal{D}\vec{q}\exp\left[\frac{i}{2}\int_{t'}^{t}\left(\dot{\vec{q}}^2-\omega^2\vec{q}^2\right)\mathrm{d}s\right]=\left(\det\frac{\partial^2 S_c}{\partial x^a\partial x'^b}\right)^{\frac{1}{2}}e^{iS_c[\vec{q}_c]}. \tag{16.2.124}$$

In other words – keeping in mind eq. (16.2.120) – the functional determinant $\left\langle\vec{0}\right|U\left|\vec{0}\right\rangle$ is also directly related to the classical action differentiated with respect to the starting and ending points of motion. Eq. (16.2.124) is not a special feature of SHO dynamics, but a rather generic feature of (the JWKB limit of) path integrals. The jump in the phase factors is also generic: it occurs whenever one of the eigenvalues of the differential operator encoded in S flips sign. □

Problem 16.8. One-particle Partition Function of SHO Recall that the energy levels of the SHO are given by

$$E_n=\left(n+\frac{1}{2}\right)\omega \tag{16.2.125}$$

in $D=1$ dimension. First show that

$$\sum_{\ell=0}^{+\infty}e^{-i(t-t')E_\ell}=\left(2i\sin\left(\omega(t-t')/2\right)\right)^{-1}. \tag{16.2.126}$$

Then demonstrate that this is consistent with eq. (16.2.46), that the 'trace' of the path integral yields the one-particle partition function. Assume $t-t'$ is not a multiple of a half-period. □

Half-Periods & Parity When $\omega(t-t')=\ell\pi$, we see the solution to path integral faces apparent infinities from all the occurrences of $1/\sin[\omega(t-t')]$ in eq. (16.2.121). This difficultly can in turn be traced to the fact that the classical solution to the SHO – with boundary conditions fixed – is no longer well defined. To see this, suppose $\dot{\vec{x}}_0$ and $\vec{x}_0$ denote respectively the initial velocity and position of the SHO at $s=t'$; then

$$\vec{q}_c[s]=\frac{\dot{\vec{x}}_0}{\omega}\sin\left[\omega(s-t')\right]+\vec{x}_0\cos\left[\omega(s-t')\right], \qquad \left(\frac{\mathrm{d}^2}{\mathrm{d}s^2}+\omega^2\right)\vec{q}_c[s]=0. \tag{16.2.127}$$

At half-periods $\omega(s-t')=\ell\pi$, the dependence on the initial velocity drops out and

$$\vec{q}_h[\omega(s-t')=\ell\pi]=\vec{x}_0(-)^\ell. \tag{16.2.128}$$

In other words, it is *not possible* to demand that, over the time duration $t-t'=\ell\pi/\omega$, a SHO particle moves from $\vec{x}_0$ to some other $\vec{x}\neq(-)^\ell\vec{x}_0$.

Let us see this from the path integral perspective. As we shall see, this result is intimately related to parity invariance of the SHO Hamiltonian. To begin, let us define in the Schrödinger picture

$$P\left|\vec{x}\right\rangle\equiv\left|-\vec{x}\right\rangle. \tag{16.2.129}$$

Note that, if $\vec{X}$ is the position operator, this is equivalent to

$$P^{-1}\vec{X}P=-\vec{X}. \tag{16.2.130}$$

Also observe that

$$P^2\left|\vec{x}\right\rangle=P\left|-\vec{x}\right\rangle=\left|\vec{x}\right\rangle \qquad \Rightarrow \qquad P^{-1}=P. \tag{16.2.131}$$

We may readily construct the symmetric and antisymmetric eigenstates of P as

$$\left|\vec{x};+\right\rangle\equiv\frac{\left|\vec{x}\right\rangle+\left|-\vec{x}\right\rangle}{\sqrt{2}} \qquad \text{and} \qquad \left|\vec{x};-\right\rangle\equiv\frac{\left|\vec{x}\right\rangle-\left|-\vec{x}\right\rangle}{\sqrt{2}}. \tag{16.2.132}$$

How does the parity operator acts on the momentum eigenstates $\{\left|\vec{k}\right\rangle\}$? We consider

$$\left\langle\vec{k}\left|P\right|\vec{x}\right\rangle=\left\langle\vec{k}\right|-\vec{x}\left\rangle=\chi e^{-i\vec{k}\cdot(-\vec{x})}=\chi e^{-i(-\vec{k})\cdot\vec{x}}=\left\langle-\vec{k}\right|\vec{x}\right\rangle. \tag{16.2.133}$$

Since this is true for any $\left|\vec{x}\right\rangle$, we must have

$$P\left|\vec{k}\right\rangle=\left|-\vec{k}\right\rangle; \tag{16.2.134}$$

and for momentum operator $\vec{p}$

$$P\vec{p}P=-\vec{p}. \tag{16.2.135}$$

Since the position and momentum operators transform in the same manner, and since the raising/lowering operators are formed from their linear combinations, this implies the $\vec{a}$ and $\vec{a}^\dagger$ in equations (12.3.10) and (12.3.11) also transform as

$$P\vec{a}P = -\vec{a}, \qquad P\vec{a}^\dagger P = -\vec{a}^\dagger. \tag{16.2.136}$$

We may use the fact that the ground state $|E_0\rangle$ is even under parity[17] to see that each higher state would alternate between odd and even under parity. For instance, if $(a^{i_\ell})^\dagger$ is the raising operator in the ℓth spatial direction,

$$\begin{aligned} P(a^{i_1})^\dagger \dots (a^{i_n})^\dagger |E_0\rangle &= P(a^{i_1})^\dagger P \cdot P(a^{i_2})^\dagger P \dots P(a^{i_{n-1}})^\dagger P \cdot P(a^{i_n})^\dagger P^2 |E_0\rangle \\ &= (-)^n (a^{i_1})^\dagger \dots (a^{i_n})^\dagger P |E_0\rangle = (-)^n (a^{i_1})^\dagger \dots (a^{i_n})^\dagger |E_0\rangle . \end{aligned} \tag{16.2.137}$$

For $\omega(t-t') = \ell\pi$, we may now analyze our path integral as follows

$$\begin{aligned} K[\omega(t-t') = \ell\pi; \vec{x}, \vec{x}'] &= \langle \vec{x}| \exp\left[-i\frac{\ell\pi}{\omega} H_{\text{SHO}}\right] |\vec{x}'\rangle , \\ &= \sum_{n_1,\dots,n_D=0}^{\infty} \langle \vec{x}|\, E_{\vec{n}}\rangle \, \langle E_{\vec{n}}|\, \vec{x}'\rangle \exp\left[-i\ell\pi\left(n_1 + \dots + n_D + \frac{D}{2}\right)\right] \\ &= \frac{1}{i^{D\cdot\ell}} \sum_{n_1,\dots,n_D=0}^{\infty} \langle \vec{x}|\, E_{\vec{n}}\rangle \, \langle E_{\vec{n}}|\, \vec{x}'\rangle \, (-)^{(n_1+\dots+n_D)\cdot\ell} \\ &= \frac{1}{i^{D\cdot\ell}} \sum_{n_1,\dots,n_D=0}^{\infty} \langle \vec{x}|\, E_{\vec{n}}\rangle \, \left\langle E_{\vec{n}}\left|P^\ell\right|\, \vec{x}'\right\rangle \\ &= \frac{1}{i^{D\cdot\ell}} \sum_{n_1,\dots,n_D=0}^{\infty} \langle \vec{x}|\, E_{\vec{n}}\rangle \, \langle E_{\vec{n}}|\, (-)^\ell \vec{x}'\rangle . \end{aligned} \tag{16.2.138}$$

But the summation is now the completeness relation:

$$K[\omega(t-t') = \ell\pi; \vec{x}, \vec{x}'] = \frac{1}{i^{D\cdot\ell}} \delta^{(D)}\left[\vec{x} - (-)^\ell \vec{x}'\right] , \tag{16.2.139}$$

where D is the number of space dimensions.

Summary The transition amplitude for the SHO system

$$\langle \vec{x}\,|\exp\left[-i(t-t')H_{\text{SHO}}\right]|\,\vec{x}'\rangle = \int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q} \exp\left[\frac{i}{2}\int_{t'}^{t}\left(\dot{\vec{q}}^2 - \omega^2\vec{q}^2\right) \mathrm{d}s\right] \tag{16.2.140}$$

is given by, for the first half-period,

$$\langle \vec{x}\,|\exp\left[-i(t-t')H_{\text{SHO}}\right]|\,\vec{x}'\rangle \tag{16.2.141}$$

$$\begin{aligned} &= e^{-iD\frac{\pi}{4}} \left|\frac{\omega}{2\pi\sin[\omega(t-t')]}\right|^{\frac{D}{2}} \exp\left[\frac{i\omega}{2\sin\left[\omega(t-t')\right]}\left((\vec{x}^2 + \vec{x}'^2)\cos\left[\omega(t-t')\right] - 2\vec{x}\cdot\vec{x}'\right)\right] \\ &\equiv K_0[t,t';\vec{x},\vec{x}'], \qquad 0 < t-t' < \frac{\pi}{\omega}; \end{aligned} \tag{16.2.142}$$

[17] Up to overall numerical/normalization constants, $\langle \vec{x}|\, E_0\rangle \propto \exp[-\omega\vec{x}^2/2]$.

and for subsequent half-periods,

$$\langle \vec{x} \,|\exp\left[-i(t-t')H_{\rm SHO}\right]|\, \vec{x}'\rangle = \frac{1}{i^D} K_0[t,t';\vec{x},\vec{x}'], \qquad \frac{\pi}{\omega} < t-t' < \frac{2\pi}{\omega}, \tag{16.2.143}$$

$$= \frac{1}{i^{2D}} K_0[t,t';\vec{x},\vec{x}'], \qquad \frac{2\pi}{\omega} < t-t' < \frac{3\pi}{\omega}, \tag{16.2.144}$$

$$= \frac{1}{i^{3D}} K_0[t,t';\vec{x},\vec{x}'], \qquad \frac{3\pi}{\omega} < t-t' < \frac{4\pi}{\omega}, \tag{16.2.145}$$

$$\ldots\ldots \tag{16.2.146}$$

[18]When the time elapsed is exactly a multiple of a half-period, $t - t' = \ell\pi/\omega$ and integer $\ell = 1, 2, 3, \ldots$,

$$\langle \vec{x} \,|\exp\left[-i(t-t')H_{\rm SHO}\right]|\, \vec{x}'\rangle = \frac{1}{i^{D\cdot\ell}} \delta^{(D)}\left[\vec{x} - (-)^\ell \vec{x}'\right]. \tag{16.2.147}$$

16.3 SHO with Time Dependent Frequency

In this section we will determine the path integral, up to overall phase factors, of the SHO but now allowing ω to depend on time.

Retarded Green's Function In this section, we wish to study the properties of the retarded Green's function of the simple harmonic oscillator with a time dependent frequency, namely:

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}t^2} + \omega[t]^2\right) G[t,t'] = \left(\frac{\mathrm{d}^2}{\mathrm{d}t'^2} + \omega[t']^2\right) G[t,t'] = \delta[t-t']; \tag{16.3.1}$$

with the constraint

$$G[t < t'] = 0. \tag{16.3.2}$$

With eq. (16.3.2), we may write

$$G[t,t'] = \Theta[t-t']\mathcal{G}[t,t']. \tag{16.3.3}$$

ODEs, Initial Value Problem We shall now argue that $\mathcal{G}$ is the homogeneous solution

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}t^2} + \omega[t]^2\right) \mathcal{G}[t,t'] = \left(\frac{\mathrm{d}^2}{\mathrm{d}t'^2} + \omega[t']^2\right) \mathcal{G}[t,t'] = 0 \tag{16.3.4}$$

with the initial values

$$\partial_t \mathcal{G}[t,t'] = -\partial_{t'} \mathcal{G}[t,t'] = 1, \qquad \mathcal{G}[t=t'] = 0. \tag{16.3.5}$$

Inserting eq. (16.3.3) into eq. (16.3.1), the ODE with respect to t reads:

$$\delta'[t-t']\mathcal{G}[t,t'] + 2\delta[t-t']\partial_t \mathcal{G}[t,t'] + \Theta[t-t']\left(\partial_t^2 + \omega^2\right)\mathcal{G}[t,t'] = 0. \tag{16.3.6}$$

[18]These phase jumps are related to the Maslov-Morse indices; see [7] for a pedagogical discussion.

Assuming $\mathcal{G}$ is smooth enough so that we may Taylor expand

$$\delta'[t-t']\mathcal{G}[t,t'] = \delta'[t-t']\left(\mathcal{G}[t=t'] + (t-t')\partial_t\mathcal{G}[t=t'] + \mathcal{O}\left[(t-t')^2\right]\right); \tag{16.3.7}$$

followed by using the distributional identity $z\delta'[z] = -\delta[z]$, we gather

$$\delta'[t-t']\mathcal{G}[t=t'] + \delta[t-t']\partial_t\mathcal{G}[t=t'] + \Theta[t-t']\left(\partial_t^2+\omega^2\right)\mathcal{G}[t,t'] = 0. \tag{16.3.8}$$

Therefore, to ensure the vanishing of the δ' and Θ terms, we require $\mathcal{G}[t=t'] = (\partial_t^2+\omega^2)\mathcal{G} = 0$; while to ensure that we are left with the desired $\delta[t-t']$ on the RHS, we must have $\partial_t\mathcal{G}[t=t'] = 1$.

A similar calculation, but now with respect to t', reveals

$$\delta'[t-t']\mathcal{G}[t,t'] - 2\delta[t-t']\partial_{t'}\mathcal{G}[t,t'] + \Theta[t-t']\left(\partial_{t'}^2+\omega^2\right)\mathcal{G}[t,t'] = 0 \tag{16.3.9}$$

$$\delta'[t-t']\mathcal{G}[t=t'] - \delta[t-t']\partial_{t'}\mathcal{G}[t,t'] + \Theta[t-t']\left(\partial_{t'}^2+\omega^2\right)\mathcal{G}[t,t'] = 0. \tag{16.3.10}$$

This leads us to conclude that $\partial_{t'}\mathcal{G}[t=t'] = -1$ and $(\partial_{t'}^2+\omega^2)\mathcal{G} = 0$.

Wronski & Solution The unique solution to equations (16.3.4) and (16.3.5) is

$$\mathcal{G}[t,t'] = -\frac{Z_1[t]Z_2[t'] - Z_2[t]Z_1[t']}{\mathrm{Wr}[Z_1,Z_2]}, \tag{16.3.11}$$

$$\mathrm{Wr}[Z_1,Z_2] \equiv Z_1\dot{Z}_2 - Z_2\dot{Z}_1; \tag{16.3.12}$$

where Z_1 and Z_2 are homogeneous solutions to the ODE, namely

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}t^2}+\omega^2\right)Z_{1,2} = 0. \tag{16.3.13}$$

Note that, under *any* invertible transformation

$$Z_{\mathrm{I}}[t] = M_{\mathrm{I}}{}^{\mathrm{J}}Y_{\mathrm{J}}[t], \tag{16.3.14}$$

$$\det M_{\mathrm{I}}{}^{\mathrm{J}} \neq 0; \tag{16.3.15}$$

where $\{Y_1, Y_2\}$ are homogeneous solutions; the solution to $\mathcal{G}$ remains invariant

$$\mathcal{G}[t,t'] = -\frac{Z_1[t]Z_2[t'] - Z_2[t]Z_1[t']}{\mathrm{Wr}[Z_1,Z_2]} = -\frac{Y_1[t]Y_2[t'] - Y_2[t]Y_1[t']}{\mathrm{Wr}[Y_1,Y_2]}. \tag{16.3.16}$$

From the Wronskian-based solution, we may see immediately that $\mathcal{G}$ is antisymmetric:

$$\mathcal{G}[t,t'] = -\mathcal{G}[t',t] \tag{16.3.17}$$

and therefore

$$\mathcal{G}[t=t'] = 0, \qquad \partial_t\partial_{t'}\mathcal{G}[t=t'] = 0. \tag{16.3.18}$$

That $\mathcal{G}$ satisfies the homogeneous solution follows from the fact that $Z_{1,2}$ are homogeneous solutions. Note that the Wronskian $\mathrm{Wr}[Z_1,Z_2]$ is time independent because there are no single derivative terms in the ODE; and thus, one may evaluate the Wronskian at any time.

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{Wr}[Z_1,Z_2] = \dot{Z}_1\dot{Z}_2 - \dot{Z}_2\dot{Z}_1 + Z_1\ddot{Z}_2 - \ddot{Z}_1Z_2 \tag{16.3.19}$$

$$= Z_1(-\omega^2)Z_2 - (-\omega^2)Z_1Z_2 = 0. \tag{16.3.20}$$

We may further check that

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{G}[t,t'] = -\frac{\dot{Z}_1[t]Z_2[t'] - \dot{Z}_2[t]Z_1[t']}{Z_1[t]\dot{Z}_2[t] - Z_2[t]\dot{Z}_1[t]} \tag{16.3.21}$$

$$\stackrel{t\to t'}{=} 1; \tag{16.3.22}$$

and likewise

$$\frac{\mathrm{d}}{\mathrm{d}t'}\mathcal{G}[t,t'] = -\frac{Z_1[t]\dot{Z}_2[t'] - Z_2[t]\dot{Z}_1[t']}{Z_1[t]\dot{Z}_2[t] - Z_2[t]\dot{Z}_1[t]} \tag{16.3.23}$$

$$\stackrel{t\to t'}{=} -1. \tag{16.3.24}$$

Kirchhoff Representation With the Green's function at hand, we may use it to solve the initial value problem

$$Z[t=t'] = x', \qquad \dot{Z}[t=t'] = \dot{x}'; \tag{16.3.25}$$

through the formula

$$Z[t] = \mathcal{G}[t,t']\dot{x}' - \partial_{t'}\mathcal{G}[t,t']x'. \tag{16.3.26}$$

This carries over to the relationship between the Heisenberg picture position operator $\vec{X}[t]$ and its 'initial' value (i.e., its Schrödinger picture counterparts) $\vec{X}[t']$ and $\vec{p}[t'] = \dot{\vec{X}}[t']$:

$$\vec{X}[t] = \mathcal{G}[t,t']\vec{p}[t'] - \partial_{t'}\mathcal{G}[t,t']\vec{X}[t']. \tag{16.3.27}$$

Note that, since $\mathcal{G}[t,t']$ is a homogeneous solution with respect to t, so is $\partial_{t'}\mathcal{G}[t,t']$. Therefore, that $Z[t]$ is a homogeneous solution is manifest; what remains is to show it satisfies the initial conditions. But since $\mathcal{G}[t=t'] = 0$ and $\partial_{t'}\mathcal{G}[t=t'] = -1$, we have

$$Z[t=t'] = 0 - (-)x'; \tag{16.3.28}$$

while using eq. (16.3.18),

$$\dot{Z}[t=t'] = \partial_t\mathcal{G}[t=t']\dot{x}' - \partial_t\partial_{t'}\mathcal{G}[t=t']x' = \dot{x}'. \tag{16.3.29}$$

Next, we may use eq. (16.3.26) to deduce the solution to the boundary value problem

$$Z[t_2] = x, \qquad Z[t_1] = x'. \tag{16.3.30}$$

It is given by

$$Z[t_1 \le s \le t_2] = \mathcal{G}[s,t_1]\frac{x + \partial_{t_1}\mathcal{G}[t_2,t_1]x'}{\mathcal{G}[t_2,t_1]} - \partial_{t_1}\mathcal{G}[s,t_1]x'. \tag{16.3.31}$$

That this is a solution follows from the fact that $\mathcal{G}[s,t_1]$ and $\partial_{t_1}\mathcal{G}[s,t_1]$ are both homogeneous solutions with respect to s, so all we have to check are

$$Z[s=t_1] = \mathcal{G}[s=t_1,t_1]\frac{x + \partial_{t_1}\mathcal{G}[t_2,t_1]x'}{\mathcal{G}[t_2,t_1]} - \partial_{t_1}\mathcal{G}[s=t_1,t_1]x' = x' \tag{16.3.32}$$

$$Z[s=t_2] = \mathcal{G}[t_2,t_1]\frac{x + \partial_{t_1}\mathcal{G}[t_2,t_1]x'}{\mathcal{G}[t_2,t_1]} - \partial_{t_1}\mathcal{G}[t_2,t_1]x' = x. \tag{16.3.33}$$

This boundary value problem has no solution for times (t_1, t_2) such that $\mathcal{G}[t_2, t_1] = 0$.

With the time derivative

$$\partial_s Z[t_1 \leq s \leq t_2] = \partial_s \mathcal{G}[s, t_1] \frac{x + \partial_{t_1} \mathcal{G}[t_2, t_1] x'}{\mathcal{G}[t_2, t_1]} - \partial_s \partial_{t_1} \mathcal{G}[s, t_1] x'. \tag{16.3.34}$$

We may construct

$$\begin{aligned} \dot{Z}[t_2] Z[t_2] - \dot{Z}[t_1] Z[t_1] = \partial_{t_2} \mathcal{G}[t_2, t_1] \frac{x^2 + \partial_{t_1} \mathcal{G}[t_2, t_1](x' \cdot x)}{\mathcal{G}[t_2, t_1]} - \partial_{t_2} \partial_{t_1} \mathcal{G}[t_2, t_1](x' \cdot x) \\ - \partial_s \mathcal{G}[s = t_1] \frac{(x \cdot x') + \partial_{t_1} \mathcal{G}[t_2, t_1] x'^2}{\mathcal{G}[t_2, t_1]} + \partial_s \partial_{t_1} \mathcal{G}[s = t_1] x'^2 \end{aligned} \tag{16.3.35}$$

$$= \partial_{t_2} \mathcal{G}[t_2, t_1] \frac{x^2 + \partial_{t_1} \mathcal{G}[t_2, t_1](x' \cdot x)}{\mathcal{G}[t_2, t_1]} - \partial_{t_2} \partial_{t_1} \mathcal{G}[t_2, t_1](x' \cdot x) - \frac{(x \cdot x') + \partial_{t_1} \mathcal{G}[t_2, t_1] x'^2}{\mathcal{G}[t_2, t_1]} \tag{16.3.36}$$

Re-arranging,

$$\dot{Z}[t_2] Z[t_2] - \dot{Z}[t_1] Z[t_1] = \frac{\partial_{t_2} \mathcal{G}[t_2, t_1] x^2 - \partial_{t_1} \mathcal{G}[t_2, t_1] x'^2}{\mathcal{G}[t_2, t_1]} + (x' \cdot x) \left\{ \frac{\partial_{t_2} \mathcal{G}[t_2, t_1] \partial_{t_1} \mathcal{G}[t_2, t_1] - 1}{\mathcal{G}[t_2, t_1]} - \partial_{t_2} \partial_{t_1} \mathcal{G}[t_2, t_1] \right\}. \tag{16.3.37}$$

A direct calculation using the Wronskian-based solution shows that

$$\frac{\partial_{t_2} \mathcal{G}[t_2, t_1] \partial_{t_1} \mathcal{G}[t_2, t_1] - 1}{\mathcal{G}[t_2, t_1]} - \partial_{t_2} \partial_{t_1} \mathcal{G}[t_2, t_1] = -\frac{2}{\mathcal{G}[t_2, t_1]}. \tag{16.3.38}$$

We arrive at

$$\dot{Z}[t_2] Z[t_2] - \dot{Z}[t_1] Z[t_1] = \frac{\partial_{t_2} \mathcal{G}[t_2, t_1] x^2 - \partial_{t_1} \mathcal{G}[t_2, t_1] x'^2}{\mathcal{G}[t_2, t_1]} - \frac{2}{\mathcal{G}[t_2, t_1]} (x' \cdot x). \tag{16.3.39}$$

JWKB Solutions We record here the JWKB solutions for $Z_{1,2}$. Whenever ω is a slowly varying function of time, we may attempt to use JWKB. The leading order solutions are

$$Z_\pm[t] = \frac{\exp\left[\pm i \int_{t'}^t \omega[s] \mathrm{d}s\right]}{\sqrt{\omega[t]}}; \tag{16.3.40}$$

and whose Wronskian is

$$Z_+[t] \dot{Z}_-[t] - Z_-[t] \dot{Z}_+[t] = -2i. \tag{16.3.41}$$

Therefore, a direct calculation reveals

$$\mathcal{G}[t, \tau] = \frac{\sin\left[\int_\tau^t \omega[s] \mathrm{d}s\right]}{\sqrt{\omega[t] \omega[\tau]}}. \tag{16.3.42}$$

Commutators Let us compute the commutator of the Heisenberg picture position operator at different times using eq. (16.3.27).

$$\begin{aligned}\left[X^i[t_1], X^j[t_2]\right] &= \left[\mathcal{G}[t_1,t']p^i[t'] - \partial_{t'}\mathcal{G}[t_1,t']X^i[t'], \mathcal{G}[t_2,t']p^j[t'] - \partial_{t'}\mathcal{G}[t_2,t']X^j[t']\right] && (16.3.43)\\ &= -\mathcal{G}[t_1,t']\partial_{t'}\mathcal{G}[t_2,t']\left[p^i[t'], X^j[t']\right] - \partial_{t'}\mathcal{G}[t_1,t']\mathcal{G}[t_2,t']\left[X^i[t'], p^j[t']\right] && (16.3.44)\\ &= i\delta^{ij}\mathcal{G}[t_1,t']\partial_{t'}\mathcal{G}[t_2,t'] - i\delta^{ij}\partial_{t'}\mathcal{G}[t_1,t']\mathcal{G}[t_2,t']. && (16.3.45)\end{aligned}$$

A direct calculation using eq. (16.3.11) reveals

$$\left[X^i[t_1], X^j[t_2]\right] = -i\delta^{ij}\mathcal{G}[t_1,t_2]. \tag{16.3.46}$$

A quick check using the equal-time commutation relation and the boundary conditions $\mathcal{G}[t,t'=t]=0$ and $\partial_{t'}\mathcal{G}[t,t'=t]=-1$: taking the time derivative with respect to t_2 and then setting $t_2=t_1=t_0$, we gather $[X_1,\dot{X}_2]_{t_2=t_1=t_0} = [X_0,p_0] = -i\delta^{ij}(-) = i\delta^{ij}$.

Time-Ordered Products

Heisenberg Picture Position Operator Let us denote the Schrödinger picture position and momentum operators as X_s and p_s respectively. If the Heisenberg picture coincides with the Schrödinger picture at t', then let us argue that the Heisenberg picture position operator $X_{\mathrm{H}}[t]$ is related to the Schrödinger position and momentum operators via

$$X_{\mathrm{H}}[t] = p_s\mathcal{G}[t,t'] - X_s\partial_{t'}\mathcal{G}[t,t']. \tag{16.3.47}$$

Because of eq. (16.3.4) we see that $\ddot{X}_H + \omega[t]^2 X_{\mathrm{H}} = 0$; moreover, because of eq. (16.3.5), we may check the Schrödinger picture is recovered at $t=t'$:

$$X_{\mathrm{H}}[t=t'] = p_s\mathcal{G}[t=t'] - X_s\partial_{t'}\mathcal{G}[t=t'] = X_s. \tag{16.3.48}$$

Path Integral The path integral is

$$\begin{aligned}\left\langle \vec{x}\left|U\right|\vec{x}'\right\rangle &= \int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q}\exp\left[\frac{i}{2}\int_{t'}^{t} \dot{\vec{q}}^2 - \omega[s]^2\vec{q}^2\mathrm{d}s\right] && (16.3.49)\\ &= e^{i\overline{S}[\vec{x},\vec{x}']}\int_{\vec{0}}^{\vec{0}} \mathcal{D}\vec{q}\exp\left[\frac{i}{2}\int_{t'}^{t} \dot{\vec{q}}^2 - \omega[s]^2\vec{q}^2\mathrm{d}s\right] && (16.3.50)\end{aligned}$$

where $\overline{S}$ is the action evaluated on the classical trajectory that begins at $\vec{q}_c[t'] = \vec{x}'$ and ends at $\vec{q}_c[t] = \vec{x}$. Now,

$$\begin{aligned}\overline{S} \equiv \frac{1}{2}\int_{t'}^{t} \dot{\vec{q}}_c^2 - \omega^2\vec{q}_c^2\mathrm{d}s &= \frac{1}{2}\left[\vec{q}_c\cdot\dot{\vec{q}}_c\right]_{t'}^{t} - \frac{1}{2}\int_{t'}^{t}\vec{q}_c\cdot\left(\frac{\mathrm{d}^2}{\mathrm{d}s^2}+\omega^2\right)\vec{q}_c\mathrm{d}s && (16.3.51)\\ &= \frac{1}{2}\left[\vec{q}_c\cdot\dot{\vec{q}}_c\right]_{t'}^{t}, && (16.3.52)\end{aligned}$$

since by assumption $\vec{q}_c$ is the classical trajectory: $(\partial_s^2+\omega^2)\vec{q}_c = 0$. Therefore,

$$\left\langle \vec{x}\left|U\right|\vec{x}'\right\rangle = e^{\frac{i}{2}\left(\vec{x}\cdot\dot{\vec{q}}_c[t] - \vec{x}'\cdot\dot{\vec{q}}_c[t']\right)}\left\langle \vec{0}\left|U\right|\vec{0}\right\rangle. \tag{16.3.53}$$

Using eq. (16.3.39), we may express the following object:

$$K[t,t';\vec{x},\vec{y}]\overline{K[t,t';\vec{x},\vec{y}']} = \left|\left\langle \vec{0}\left|U\right|\vec{0}\right\rangle\right|^2 \tag{16.3.54}$$
$$\times \exp\left[\frac{i}{2}\left(\frac{\partial_t \mathcal{G}[t,t']\vec{x}^2 - \partial_{t'}\mathcal{G}[t,t']\vec{y}^2}{\mathcal{G}[t,t']} - \frac{2}{\mathcal{G}[t,t']}(\vec{x}\cdot\vec{y})\right)\right]$$
$$\times \exp\left[-\frac{i}{2}\left(\frac{\partial_t \mathcal{G}[t,t']\vec{x}^2 - \partial_{t'}\mathcal{G}[t,t']\vec{y}'^2}{\mathcal{G}[t,t']} - \frac{2}{\mathcal{G}[t,t']}(\vec{x}\cdot\vec{y}')\right)\right]$$
$$= |\left\langle \vec{0}\left|U\right|\vec{0}\right\rangle|^2 \tag{16.3.55}$$
$$\times \exp\left[\frac{i}{2}\left(\frac{\partial_{t'}\mathcal{G}[t,t']}{\mathcal{G}[t,t']}(\vec{y}'^2 - \vec{y}^2) - \frac{2}{\mathcal{G}[t,t']}\vec{x}\cdot(\vec{y}-\vec{y}')\right)\right]$$

We may compute the functional determinant $|\left\langle \vec{0}\left|U\right|\vec{0}\right\rangle|^2$ – which depends on time but not on space – as follows. Notice

$$\int_{\mathbb{R}^D} \mathrm{d}^D\vec{x} K[t,t';\vec{x},\vec{y}]\overline{K[t,t';\vec{x},\vec{y}']} = \int_{\mathbb{R}^D} \mathrm{d}^D\vec{x}\left\langle \vec{y}'\left|U^\dagger\right|\vec{x}\right\rangle\left\langle \vec{x}\left|U\right|\vec{y}\right\rangle = \delta^{(D)}[\vec{y}'-\vec{y}]$$
$$= |\left\langle \vec{0}\left|U\right|\vec{0}\right\rangle|^2 \int_{\mathbb{R}^D}\mathrm{d}^D\vec{x}\exp\left[-\frac{i}{\mathcal{G}[t,t']}\vec{x}\cdot(\vec{y}-\vec{y}')\right]$$
$$= |\left\langle \vec{0}\left|U\right|\vec{0}\right\rangle|^2 |\mathcal{G}[t,t']|^D (2\pi)^D\delta^{(D)}[\vec{y}-\vec{y}'] \tag{16.3.56}$$

We therefore have

$$K[t,t';\vec{x},\vec{y}]\overline{K[t,t';\vec{x},\vec{y}']} = |2\pi\mathcal{G}[t,t']|^{-D}\exp\left[\frac{i}{2}\frac{\partial_{t'}\mathcal{G}[t,t']}{\mathcal{G}[t,t']}(\vec{y}'^2-\vec{y}^2) - \frac{i}{\mathcal{G}[t,t']}\vec{x}\cdot(\vec{y}-\vec{y}')\right]. \tag{16.3.57}$$

17 Variational Method: Examples

Theorem The basic premise behind the variational method is:

> The expectation value of the Hamiltonian H with respect to any physical state $|\psi\rangle$ is always greater or equal to the lowest, i.e., ground state, energy E_0.

$$E_0 \leq \frac{\langle\psi\left|H\right|\psi\rangle}{\langle\psi|\,\psi\rangle}, \qquad \forall\,|\psi\rangle\,. \tag{17.0.1}$$

It's possible to obtain such bounds on excited states, if you know how to construct trial states that are orthogonal to all the lower lying ones. For instance, if $|E_0\rangle$ is the ground state, E_1 is the first excited state energy level, and $\langle\psi|\,E_0\rangle = 0$; then

$$E_1 \leq \frac{\langle\psi\left|H\right|\psi\rangle}{\langle\psi|\,\psi\rangle}, \qquad \forall\,|\psi\rangle\,. \tag{17.0.2}$$

More generally, if $\langle\psi|\, E_0\rangle = \ldots \langle\psi|\, E_{n-1}\rangle = 0$, where $\{E_i | i = 0, \ldots, n-1\}$ are the first n energy levels, then

$$E_n \leq \frac{\langle\psi\,|H|\,\psi\rangle}{\langle\psi|\,\psi\rangle}, \qquad \forall\,|\psi\rangle\,. \tag{17.0.3}$$

Variational Method This means, to estimate E_0, we may cook up some trial state $|\psi;\{\alpha_{\rm I}\}\rangle$ with parameters $\{\alpha_{\rm I}\}$; and compute $\langle\psi;\{\alpha_{\rm I}\}\,|H|\,\psi;\{\alpha_{\rm I}\}\rangle\,/\,\langle\psi;\{\alpha_{\rm I}\}|\,\psi;\{\alpha_{\rm I}\}\rangle$. Then we may minimize this quantity – this is why it is dubbed the 'variational method' – with respect to the $\{\alpha_{\rm I}\}$ and use the ensuing minimum $\langle\psi;\{\alpha_{\rm I}\}\,|H|\,\psi;\{\alpha_{\rm I}\}\rangle\,/\,\langle\psi;\{\alpha_{\rm I}\}|\,\psi;\{\alpha_{\rm I}\}\rangle$ as an estimate E_0. Of course, there is some art involved here, since the form of the trial state is only constrained by the practitioner's creativity.

1D SHO Let us use a gaussian with an arbitrary width, namely

$$\langle x|\,\psi;a\rangle = \exp(-(a/2)x^2), \tag{17.0.4}$$

as the trial ground state in the 1D simple harmonic oscillator. Via a direct calculation,

$$H = \frac{p^2}{2m} + \frac{1}{2}\omega^2 x^2, \tag{17.0.5}$$

$$\frac{\langle\psi;a\,|H|\,\psi;a\rangle}{\langle\psi;a|\,\psi;a\rangle} = \frac{\int_{\mathbb{R}} e^{-(ax^2)/2}\left(-\frac{\partial_x^2}{2m} + \frac{1}{2}\omega^2x^2\right)e^{-(ax^2)/2}\mathrm{d}x}{\int_{\mathbb{R}} e^{-ax^2}\mathrm{d}x} \tag{17.0.6}$$

$$= \frac{a^2+\omega^2}{4a} \tag{17.0.7}$$

Minimizing this means

$$\frac{\partial}{\partial a}\frac{a^2+\omega^2}{4a} = 0; \tag{17.0.8}$$

whose solutions are $a = \pm\omega$. Since we want the positive root – otherwise the gaussian will blow up at infinity – we then recover the exact ground state energy

$$E_0[\text{est.}] = \left.\frac{a^2+\omega^2}{4a}\right|_{a=\omega} = \frac{\omega}{2}. \tag{17.0.9}$$

Hydrogen Atom Let us use a decaying exponential with an arbitrary width, namely

$$\langle x|\,\psi;a\rangle = \exp(-(a/2)r), \tag{17.0.10}$$

as the trial ground state in the hydrogen-like atom. Via a direct calculation,

$$H = \frac{p^2}{2m} - \frac{Ze^2}{r}, \tag{17.0.11}$$

$$\frac{\langle\psi;a\,|H|\,\psi;a\rangle}{\langle\psi;a|\,\psi;a\rangle} = \frac{\int_0^{+\infty} e^{-ar/2}\left(-\frac{\vec{\nabla}^2}{2m} - \frac{Ze^2}{r}\right)e^{-ar/2}\mathrm{d}r}{\int_0^{\infty} e^{-ar}\mathrm{d}r} \tag{17.0.12}$$

$$= \frac{a(a-4e^2mZ)}{8m} \tag{17.0.13}$$

Minimizing this means

$$\frac{\partial}{\partial a}\frac{a(a-4e^2mZ)}{8m}=0; \tag{17.0.14}$$

whose solution is $a=2me^2Z$. We then recover the exact ground state energy

$$E_0[\text{est.}]=\left.\frac{a(a-4e^2mZ)}{8m}\right|_{a=2me^2Z}=-\frac{(Ze^2)^2}{2}m. \tag{17.0.15}$$

Problem 17.1. Consider the quartic oscillator, defined by

$$H=\frac{P^2}{2m}+\frac{\lambda}{4!}X^4. \tag{17.0.16}$$

Assume the ground state is even under parity transformations. Estimate the ground state and the first excited state energy levels. □

18 Rayleigh-Schrödinger Perturbation Theory

18.1 1D SHO perturbed with a x^4 potential

Let us consider

$$H=\frac{p^2}{2}+\frac{1}{2}\omega^2x^2+\lambda x^4. \tag{18.1.1}$$

We may split this Hamiltonian up into the SHO plus the x^4 term.

$$H=H_0+H_1, \tag{18.1.2}$$

$$H_0\equiv\frac{p^2}{2}+\frac{1}{2}\omega^2x^2, \tag{18.1.3}$$

$$H_1\equiv\lambda x^4. \tag{18.1.4}$$

First Order Shift of Ground State Energy We may compute the first order shift in the ground state energy

$$\langle x|\,E_0\rangle=\sqrt{\frac{\omega}{\pi}}\exp\left(-\frac{\omega}{2}x^2\right) \tag{18.1.5}$$

$$\delta_1E_0=\lambda\left\langle E_0\left|X^4\right|E_0\right\rangle=\lambda\int_{\mathbb{R}}x^4\frac{\omega}{\pi}\exp\left(-\omega x^2\right)\mathrm{d}x \tag{18.1.6}$$

$$=\lambda\frac{\omega}{\pi}\partial_\omega^2\sqrt{\frac{\pi}{\omega}}=\frac{3\lambda}{4\sqrt{\pi}\omega^{\frac{3}{2}}}. \tag{18.1.7}$$

Why does this answer blow up with $\omega\to0$? Can you estimate, when does perturbation theory break down?

18.2 Hydrogen-like Atoms

18.2.1 Stark Effect

Quadratic Stark Effect of Ground State Let us consider immersing a hydrogen-like atom in a constant electric field, which we shall denote as

$$\vec{E} = E\hat{z} = -\vec{\nabla}(-Ez). \tag{18.2.1}$$

The Hamiltonian is

$$H = H_0 + H_1, \tag{18.2.2}$$

$$H_0 \equiv \frac{\vec{p}^2}{2m} - \frac{Ze^2}{r}, \tag{18.2.3}$$

$$H_1 \equiv -eEz. \tag{18.2.4}$$

Ignoring spin, the ground state of hydrogen is non-degenerate. The first order correction is

$$\delta_1 E_0 = -eE \left\langle \bar{E}_1 \right| z \left| \bar{E}_1 \right\rangle = 0. \tag{18.2.5}$$

because of parity. There is no linear Stark effect for the ground state.

Let's do quadratic order. We need to compute

$$\delta_2 E_0 = -(eE)^2 \sum_{s>1} \frac{|\left\langle \bar{E}_s \right| Z \left| \bar{E}_0 \right\rangle|^2}{\bar{E}_s - \bar{E}_1}. \tag{18.2.6}$$

The sum must include all excited bound states as well as the integral over the continuum states. Following Sakurai, we may estimate this sum as follows

$$\delta_2 E_0 < -\frac{(eE)^2}{\bar{E}_2 - \bar{E}_1} \sum_{s>1} \left\langle \bar{E}_1 \right| Z \left| \bar{E}_s \right\rangle \left\langle \bar{E}_s \right| Z \left| \bar{E}_1 \right\rangle \tag{18.2.7}$$

$$= -\frac{(eE)^2}{\bar{E}_2 - \bar{E}_1} \left\langle \bar{E}_1 \right| Z^2 \left| \bar{E}_1 \right\rangle. \tag{18.2.8}$$

By spherical symmetry of the ground state

$$\left\langle \bar{E}_1 \right| Z^2 \left| \bar{E}_1 \right\rangle = \left\langle \bar{E}_1 \right| Y^2 \left| \bar{E}_1 \right\rangle = \left\langle \bar{E}_1 \right| X^2 \left| \bar{E}_1 \right\rangle = \frac{1}{3} \left\langle \bar{E}_1 \right| r^2 \left| \bar{E}_1 \right\rangle = \frac{a_{\mathrm{B}}^2}{3}. \tag{18.2.9}$$

whereas $\bar{E}_2 - \bar{E}_1 = (3e^2/(8a_{\mathrm{B}}))$. Hence

$$0 > \delta_2 E_0 > -\frac{8a_{\mathrm{B}}^3}{9}(eE)^2. \tag{18.2.10}$$

Linear Stark Effect for Excited States As long as the electric field is large enough so that the Stark effect overwhelms the spin-orbit interactions, the excited states are degenerate – remember $0 \leq \ell \leq n-1$ and $-\ell \leq m \leq m$ – we need to apply degenerate perturbation theory. In particular, we need to diagonalize

$$\left\langle n; \ell_1, m_1 \right| X^3 \left| n; \ell_2, m_2 \right\rangle = \left\langle n; \ell_1, m_1 \right| X_1^0 \left| n; \ell_2, m_2 \right\rangle. \tag{18.2.11}$$

We recognize the third component of a vector to be the $m = 0$ component of its $\ell = 1$ spherical tensor counterpart. Hence

$$m_1 = m_2. \tag{18.2.12}$$

Moreover, by the Wigner-Eckart theorem, we know that such a matrix element is proportional to the Clebsch-Gordon coefficient arising from adding angular momentum 1 and ℓ_2 to obtain ℓ_1.

$$\begin{aligned}\left\langle n; \ell_1, m_1 \left| X^3 \right| n; \ell_2, m_2 \right\rangle = \langle \ell_1 \ m_{1,2}; 1 \ \ell_2 | 1 \ 0, \ell_2 \ m_{1,2} \rangle \\ \times \langle n; \ell_1 || X^0_1 || n; \ell_2 \rangle.\end{aligned} \tag{18.2.13}$$

which in turn informs us, for $\ell_2 = 0$,

$$\ell_1 = 1; \tag{18.2.14}$$

and for $\ell_2 \geq 1$,

$$\ell_1 = \ell_2 - 1, \ell_2, \ell_2 + 1 \leq n - 1. \tag{18.2.15}$$

Finally, under parity transformations,[19]

$$\left\langle n; \ell_1, m_1 \left| P X^3 P \right| n; \ell_2, m_2 \right\rangle = - \left\langle n; \ell_1, m_1 \left| X^3 \right| n; \ell_2, m_2 \right\rangle \tag{18.2.16}$$

$$= (-)^{\ell_1 + \ell_2} \left\langle n; \ell_1, m_1 \left| X^3 \right| n; \ell_2, m_2 \right\rangle . \tag{18.2.17}$$

That means we require $\ell_1 + \ell_2 + 1$ to be even – for e.g., $\ell_1 \neq \ell_2$. Since $\ell_{1,2}$ can differ by at most one,

$$|\ell_1 - \ell_2| = 1. \tag{18.2.18}$$

Let us examine the $n = 2$ states. Here, $\ell_2 = 0, 1$. But because ℓ cannot be greater than unity, we have

$$\ell_1 = 0, 1. \tag{18.2.19}$$

Since $\ell_1 \neq \ell_2$, we can only have $(\ell_1 = 1, \ell_2 = 0)$ or $(\ell_1 = 1, \ell_2 = 0)$. Moreover, this also teaches us $m_1 = m_2 = 0$. The relevant un-perturbed eigenstates are

$$\langle r, \theta, \phi | \, n = 2; \ell = 0 \ m = 0 \rangle = \frac{2 - r/a_{\rm B}}{(2a_{\rm B})^{3/2}} \exp\left(-\frac{r}{2a_{\rm B}} \right) Y^0_0 \tag{18.2.20}$$

$$\langle r, \theta, \phi | \, n = 2; \ell = 1 \ m = 0 \rangle = \frac{1}{(2a_{\rm B})^{3/2}} \frac{r}{3^{1/2} a_{\rm B}} \exp\left(-\frac{r}{2a_{\rm B}} \right) Y^0_1(\theta, \phi) \tag{18.2.21}$$

$$Y^0_0 = \frac{1}{\sqrt{4\pi}}, \qquad Y^0_1(\theta, \phi) = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos\theta. \tag{18.2.22}$$

Via a direct calculation, we may deduce

$$\begin{aligned}\left\langle n = 2; \ell = 0 \ m = 0 \left| X^3 \right| n = 2; \ell = 1 \ m = 0 \right\rangle = \left\langle n = 2; \ell = 1 \ m = 0 \left| X^3 \right| n = 2; \ell = 0 \ m = 0 \right\rangle \\ = -3a_{\rm B}.\end{aligned} \tag{18.2.23}$$

[19] Very similar considerations apply for dipole radiative transitions.

The corresponding eignenstates and eigenvalues of $H_1 = -eEX^3$ is therefore

$$H_1 \left|\pm 3eEa_{\rm B}\right\rangle = \pm 3eEa_{\rm B} \left|\pm 3eEa_{\rm B}\right\rangle \tag{18.2.24}$$

$$\left|\pm 3eEa_{\rm B}\right\rangle = \frac{1}{\sqrt{2}} \left(\left|n=2;\ell=1\ m=0\right\rangle \pm \left|n=2;\ell=0\ m=0\right\rangle\right). \tag{18.2.25}$$

Remember the shift in energy is precisely these eigenvalues

$$\delta_1 E_{n=2} = \pm 3eEa_{\rm B}. \tag{18.2.26}$$

Symmetry vs degeneracy The degeneracy is lifted for the states involving $|\ell = 0, m = 0\rangle$ and $|\ell = 1, m = 0\rangle$. Physically speaking, we may attribute this to the electric field breaking the original rotational symmetry of the H_0. On the other hand, notice the $|\ell = 1, m = \pm 1\rangle$ states still yield un-perturbed energies up to first order; i.e., their degeneracy is not lifted. Physically, we may attribute this remaining degeneracy to the residual axial symmetry under rotation about the direction parallel to $\vec{E}$.

Caution We are ignoring spin here. Actually, the spin-orbit interaction involving the operator $\vec{L} \cdot \vec{S}$ can be more important that the $-eE\vec{X} \cdot \vec{E}$ dipole interaction here, for very weak electric fields. So the results here are really only valid for strong enough electric fields – but not too strong that perturbation theory itself breaks down!

Problem 18.1. Linear Stark Effect for $n = 3$ Still ignoring spin, work out the first order shift in the $n = 3$ energy levels due to the Stark effect. □

Relativistic Corrections In relativity, the kinetic energy is

$$K = \sqrt{\vec{p}^2 + m^2} - m^2 = \frac{\vec{p}^2}{2m} - \frac{(\vec{p}^2)^2}{8m^3} + \mathcal{O}(\vec{p}^6/m^5). \tag{18.2.27}$$

If we consider hydrogen-like atoms,

$$H = H_0 + H_1 \tag{18.2.28}$$

$$H_0 = \frac{\vec{p}^2}{2m} - \frac{Ze^2}{r} \tag{18.2.29}$$

$$H_1 = -\frac{(\vec{p}^2)^2}{8m^3}; \tag{18.2.30}$$

we may compute the first order corrections to the energy levels due to the relativistic correction in H_1. Let's begin with the ground state, which is non-degenerate if we ignore spin. The ground state is

$$\left\langle \vec{x} \right| \bar{E}_1 \rangle = \frac{\exp(-r/a_{\rm B})}{\sqrt{\pi} a_{\rm B}^{3/2}}, \qquad a_{\rm B} \equiv (me^2 Z)^{-1} \tag{18.2.31}$$

$$\bar{E}_n = -\frac{m}{2n^2}(e^2 Z)^2 = -\frac{1}{2m(na_{\rm B})^2} \approx -(13.6{\rm eV})\frac{Z^2}{n^2}. \tag{18.2.32}$$

We find that

$$\begin{aligned}\delta_1 E_1 &= \left\langle \bar{E}_1 \right| H_1 \left| \bar{E}_1 \right\rangle \\ &= -\left\langle \bar{E}_1 \left| \frac{(\vec{p}^2)^2}{2m(2m)^2} \right| \bar{E}_1 \right\rangle \qquad (18.2.33) \\ &= -\frac{1}{2m} \left\langle \bar{E}_1 \right| \left(H_0 + \frac{Ze^2}{r} \right)^2 \left| \bar{E}_1 \right\rangle \qquad (18.2.34) \\ &= -\frac{1}{2m} \left(\bar{E}_0^2 + 2\bar{E}_0 \left\langle \bar{E}_1 \right| \frac{Ze^2}{r} \left| \bar{E}_1 \right\rangle + \left\langle \bar{E}_1 \right| \frac{(Ze^2)^2}{r^2} \left| \bar{E}_1 \right\rangle \right). \qquad (18.2.35)\end{aligned}$$

A direct calculation would tell us

$$\left\langle \bar{E}_1 \right| \frac{Ze^2}{r} \left| \bar{E}_1 \right\rangle = -2\bar{E}_1 \qquad (18.2.36)$$

$$\left\langle \bar{E}_1 \right| \frac{(Ze^2)^2}{r^2} \left| \bar{E}_1 \right\rangle = 8\bar{E}_1^2. \qquad (18.2.37)$$

Therefore

$$\delta_1 E_1 = -\frac{5}{8}(e^2 Z)^4 m = \frac{5}{4}(e^2 Z)^2 \bar{E}_1. \qquad (18.2.38)$$

Note that H_1 is rotationally symmetric. So it is already diagonal in the $|n;\ell,m\rangle$ basis. Following Sakurai, we first write

$$\begin{aligned}\delta_1 E_{n,\ell,m} &= \langle n;\ell,m \left| H_1 \right| n;\ell,m \rangle \\ &= -\left\langle n;\ell,m \left| \frac{(\vec{p}^2)^2}{2m(2m)^2} \right| n;\ell,m \right\rangle \qquad (18.2.39) \\ &= -\frac{1}{2m} \langle n;\ell,m| \left(H_0 + \frac{Ze^2}{r} \right)^2 |n;\ell,m\rangle \qquad (18.2.40) \\ &= -\frac{1}{2m} \left(\bar{E}_0^2 + 2\bar{E}_0 \langle n;\ell,m| \frac{Ze^2}{r} |n;\ell,m\rangle + \langle n;\ell,m| \frac{(Ze^2)^2}{r^2} |n;\ell,m\rangle \right). \qquad (18.2.41)\end{aligned}$$

$$\langle n;\ell,m| \frac{Ze^2}{r} |n;\ell,m\rangle = -2\bar{E}_n \qquad (18.2.42)$$

$$\langle n;\ell,m| \frac{(Ze^2)^2}{r^2} |n;\ell,m\rangle = \frac{4n}{\ell+1/2}\bar{E}_n^2. \qquad (18.2.43)$$

$$\delta_1 E_{n,\ell,m} = -\frac{m}{2}(Ze^2)^4 \left(\frac{1}{n^3(\ell+1/2)} - \frac{3}{4n^4} \right) \qquad (18.2.44)$$

18.2.2 Spin-Orbit & Fine Structure

Spin-Orbit & Fine Structure[20] Consider a multi-electron atom, such that the zeroth order Hamiltonian of one of its electrons is

$$H_0 = \frac{\vec{p}^2}{2m} + V_c(r). \qquad (18.2.45)$$

[20]This discussion is modeled after that in Sakurai [3].

Suppose the eigenstates are

$$\langle r, \theta, \phi |\, n; \ell, m \rangle = R_n^\ell(r) Y_\ell^m(\theta, \phi). \tag{18.2.46}$$

The spin-orbit interaction, which goes as the magnetic moment dotted into the $\vec{B}-$field (i.e., $-\vec{\mu} \cdot \vec{B}$), is

$$H_1 = \frac{1}{2m_e^2} \frac{1}{r} \frac{\mathrm{d}V_c}{\mathrm{d}r} \vec{L} \cdot \vec{S} \tag{18.2.47}$$

$$= \frac{1}{2m_e^2} \frac{1}{r} \frac{\mathrm{d}V_c}{\mathrm{d}r} \frac{1}{2} \left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2 \right), \tag{18.2.48}$$

where the $\mathrm{d}V/\mathrm{d}r$ is related to the electric field experienced by the moving charge as it orbits the nucleus.

The eigenstates that render H_1 diagonal therefore involve the total angular momentum eigenstates $\{|n; j = \ell \pm 1/2 \; m; \ell \; 1/2\rangle\}$. They can be constructed using $\{n; \ell, m\}$ above, tensor-ed with the spin degrees of freedom:

$$\left| n; j = \ell \pm \frac{1}{2} \; m; \ell \; \frac{1}{2} \right\rangle = \sum_{m = m_\ell + m_s} |n; \ell, m_\ell\rangle \otimes \left| \frac{1}{2}, m_s \right\rangle \left\langle \ell \; m_\ell, \frac{1}{2} \; m_s \right| j = \ell \pm \frac{1}{2} \; m; \ell \; \frac{1}{2} \right\rangle. \tag{18.2.49}$$

The energy shift is therefore

$$\begin{aligned} \delta_1 E_{n,j,\ell} &= \left\langle n; j = \ell \pm \frac{1}{2} \; m; \ell \; \frac{1}{2} \right| H_1 \left| n; j = \ell \pm \frac{1}{2} \; m; \ell \; \frac{1}{2} \right\rangle \\ &= \frac{1}{4m_e^2} \left(j(j+1) - \ell(\ell+1) - \frac{1}{2}\left(\frac{1}{2} + 1\right) \right) \left\langle n; \ell \left| \frac{1}{r} \frac{\mathrm{d}V_c}{\mathrm{d}r} \right| n; \ell \right\rangle \\ &= \frac{1}{4m_e^2} \left\langle n; \ell \left| \frac{1}{r} \frac{\mathrm{d}V_c}{\mathrm{d}r} \right| n; \ell \right\rangle \times \begin{cases} \ell & \text{for } j = \ell + \frac{1}{2} \\ -(\ell+1) & \text{for } j = \ell - \frac{1}{2} \end{cases} \end{aligned} \tag{18.2.50}$$

$$\left\langle n; \ell \left| \frac{1}{r} \frac{\mathrm{d}V_c}{\mathrm{d}r} \right| n; \ell \right\rangle = \int_0^\infty \overline{R_n^\ell(r)} \frac{1}{r} \frac{\mathrm{d}V_c(r)}{\mathrm{d}r} R_n^\ell(r) r^2 \mathrm{d}r. \tag{18.2.51}$$

According to Sakurai, this is known as Lande's interval rule. If V_c is simply the Coulomb potential; setting $\ell = 0$ actually yields the result obtained from the Darwin term. See Sakurai for a specific discussion on sodium.

18.2.3 Zeeman Effect

Zeeman effect The vector potential associated with a constant magnetic field $\vec{B}$ is

$$A^i = \frac{1}{2} (\vec{B} \times \vec{x})^i = \frac{1}{2} \epsilon^{ijk} B^j x^k. \tag{18.2.52}$$

Check:

$$(\vec{\nabla} \times \vec{A})^a = \partial_b \left(\epsilon^{abc} A^c \right) \tag{18.2.53}$$

$$= \frac{1}{2}\partial_b \left(\epsilon^{abc}\epsilon^{cjk} B^j x^k\right) \tag{18.2.54}$$

$$= \frac{1}{2}(\delta^a_j \delta^b_k - \delta^a_k \delta^b_j) B^j \delta^k_b = \frac{1}{2}(3\delta^a_j - \delta^a_j) B^j \tag{18.2.55}$$

$$= B^a \tag{18.2.56}$$

If we include spin-orbit interactions, the Hamiltonian in the presence of a vector potential is

$$H = (2m_e)^{-1}\left(\vec{p} - e\vec{A}\right)^2 + \frac{1}{2m^2}\frac{V'(r)}{r}\vec{L}\cdot\vec{S} + V \tag{18.2.57}$$

$$= (2m_e)^{-1}\left(\vec{p}^2 + e^2\vec{A}^2 - e(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p})\right) + V. \tag{18.2.58}$$

It turns out, in this case, that $\vec{A}\cdot\vec{p} = \vec{p}\cdot\vec{A}$.

$$\left\langle \vec{x}\left|\vec{p}\cdot\vec{A}\right|\psi\right\rangle = -i\vec{\nabla}\cdot\left(\vec{A}\left\langle\vec{x}\right|\psi\right\rangle\right) \tag{18.2.59}$$

$$= -i\left(\vec{\nabla}\cdot\vec{A} + \vec{A}\cdot\vec{\nabla}\right)\left\langle\vec{x}\right|\psi\right\rangle \tag{18.2.60}$$

$$\left\langle \vec{x}\left|\vec{A}\cdot\vec{p}\right|\psi\right\rangle = -i\vec{A}\cdot\vec{\nabla}\left\langle\vec{x}\right|\psi\right\rangle \tag{18.2.61}$$

$$= -\frac{i}{2}\epsilon^{abc}B^b x^c \partial_a \left\langle\vec{x}\right|\psi\right\rangle = -\frac{i}{2}\epsilon^{bca}B^b x^c \partial_a \left\langle\vec{x}\right|\psi\right\rangle \tag{18.2.62}$$

$$= -\frac{i}{2}\vec{B}\cdot\left(\vec{x}\times\vec{\nabla}\right)\left\langle\vec{x}\right|\psi\right\rangle = \frac{1}{2}\left\langle\vec{x}\left|\vec{B}\cdot\vec{L}\right|\psi\right\rangle. \tag{18.2.63}$$

We may compute

$$\vec{\nabla}\cdot\vec{A} = \frac{1}{2}\partial_a(\epsilon^{abc}B^b x^c) = \frac{1}{2}\epsilon^{abc}B^b\delta^c_a = 0. \tag{18.2.64}$$

Moreover, note that

$$\vec{A}^2 = \frac{1}{4}\epsilon^{aij}\epsilon^{abc}B^i B^b x^j x^c = \frac{1}{4}(\delta^i_b\delta^j_c - \delta^i_c\delta^j_b)B^i B^b x^j x^c \tag{18.2.65}$$

$$= \frac{1}{4}\left(B^2r^2 - (\vec{B}\cdot\vec{x})^2\right). \tag{18.2.66}$$

Weak B field We need to include the interaction between $\vec{B}$ and spin; i.e., $-\vec{\mu}\cdot\vec{B} = -(ge/(2m_e))\vec{B}\cdot\vec{S}$ with $g \approx 2$. The Hamiltonian at this point reads

$$H' = H_0 + H_1 + H_2, \tag{18.2.67}$$

$$H_0 \equiv \frac{\vec{p}^2}{2m_e} + V + \frac{1}{2m^2}\frac{V'(r)}{r}\vec{L}\cdot\vec{S} \tag{18.2.68}$$

$$H_1 \equiv -\frac{e}{2m_e}\vec{B}\cdot(\vec{L} + g\vec{S}) \tag{18.2.69}$$

$$H_2 \equiv \frac{e^2}{8m}\left(B^2r^2 - (\vec{B}\cdot\vec{x})^2\right). \tag{18.2.70}$$

The eigenstates of H_0 may be labeled by (n, j, m, ℓ), where n is the Bohr-like energy label, j is the total angular momentum, m is its azimuthal number, and ℓ is the orbital angular momentum. Let us use the fact that $\vec{L} + g\vec{S}$ is a vector operator to assert

$$\left\langle n, j, m_1, \ell \left| B^i (L^i + gS^i) \right| n, j, m_2, \ell \right\rangle = \chi_{n,j,\ell} \left\langle j, m \left| J^i \right| j, m \right\rangle B^i, \tag{18.2.71}$$

$$\chi_{n,j,\ell} \equiv \frac{\left\langle n, j, m_1, \ell \left| \vec{J}(\vec{L} + g\vec{S}) \right| n, j, m_2, \ell \right\rangle}{j(j+1)}, \tag{18.2.72}$$

where $\chi_{n,j,\ell}$ is a constant independent of the ms.

$$\chi_{n,j,\ell} = \frac{\left\langle n, j, m_1, \ell \left| \vec{L}^2 + \vec{L} \cdot \vec{S} + g\vec{S}^2 + g\vec{L} \cdot \vec{S} \right| n, j, m_2, \ell \right\rangle}{j(j+1)} \tag{18.2.73}$$

$$= (j(j+1))^{-1} \left\{ \ell(\ell+1) + g\frac{1}{2}\frac{3}{2} + \frac{1+g}{2} \left\langle n, j, m_1, \ell \left| \vec{J}^2 - \vec{L}^2 - \vec{S}^2 \right| n, j, m_2, \ell \right\rangle \right\} \tag{18.2.74}$$

$$= (j(j+1))^{-1} \left\{ \ell(\ell+1) + g\frac{1}{2}\frac{3}{2} + \frac{1+g}{2} \left(j(j+1) - \ell(\ell+1) - \frac{3}{4} \right) \right\} \tag{18.2.75}$$

$$= 1 + (g-1)\frac{j(j+1) - \ell(\ell+1) + 3/4}{2j(j+1)} = \chi_{j,\ell}. \tag{18.2.76}$$

We see that $\chi_{n,j,\ell}$ in fact does not depend on n.

Problem 18.2. Verify that

$$\chi_{j=\ell\pm1/2,\ell} = 1 \pm \frac{g-1}{2\ell+1} \approx 1 \pm \frac{1}{2\ell+1}. \tag{18.2.77}$$

Remember: for a single electron $j = \ell \pm 1/2$. □

The expectation value of H_1 may now be expressed as

$$\langle n, j, m, \ell \left| H_1 \right| n, j, m, \ell \rangle = -\frac{e g_{j,\ell}}{2m_e} \left\langle n, j, m, \ell \left| \vec{B} \cdot \vec{J} \right| n, j, m, \ell \right\rangle. \tag{18.2.78}$$

Choosing $\vec{B}$ to be parallel to the $z-$axis, $\vec{B} = B\widehat{z}$, we must have

$$\delta_1 E_{n,j=\ell\pm1/2,m,\ell} = \langle n, j = \ell \pm 1/2, m, \ell \left| H_1 \right| n, j = \ell \pm 1/2, m, \ell \rangle \tag{18.2.79}$$

$$= -\frac{eB}{2m_e} \left(1 \pm \frac{g-1}{2\ell+1} \right) m \approx -\frac{eB}{2m_e} \left(1 \pm \frac{1}{2\ell+1} \right) m. \tag{18.2.80}$$

For sodium, when $\vec{B} = 0$, Weinberg tells us the D_1 lines are due to

$$^3p_{1/2} \to {}^3s_{1/2} \tag{18.2.81}$$

$$(n = 3, \ell = 1, j = 1/2 = \ell - 1/2) \to (n = 3, \ell = 0, j = 1/2 = \ell + 1/2). \tag{18.2.82}$$

This means when a $\vec{B}$ field is turned on, the D_1 line is split into

$$\Delta E(m \to m') = -\frac{eB}{2m_e} \left(\left(1 - \frac{1}{3} \right) m - (1+1)\, m' \right) \tag{18.2.83}$$

$$= -\frac{eB}{2m_e} \left(\frac{2}{3} m - 2m' \right). \tag{18.2.84}$$

Here, $m = \pm 1/2 = m'$. Therefore there are 4 possible transitions.

$$\Delta E(\pm 1/2 \to \pm 1/2) = \mp \frac{eB}{2m_e}\left(\frac{1}{3} - 2\right) = \mp \frac{eB}{2m_e}\frac{2}{3} \tag{18.2.85}$$

$$\Delta E(\pm 1/2 \to \mp 1/2) = \mp \frac{eB}{2m_e}\left(\frac{1}{3} + 2\right) = \mp \frac{eB}{2m_e}\frac{4}{3}. \tag{18.2.86}$$

Weinberg tells us that these results allowed Lorentz (who set $g = 1$) to conclude from Zeeman's data to recognize that the particles responsible for these radiative transitions must have a e/m roughly 3 orders of magnitude larger than those in electrolysis.

Problem 18.3. Verify Weinberg eq. 5.2.11. Then, recall from Wigner-Eckart that $\langle j, m_1 \left| J^i \right| j, m_2 \rangle$ is non-zero only when $|m_1 - m_2| \leq 1$. Use this to explain/verify Weinberg equations 5.2.14 through 5.2.16. □

Strong B field Thus far, we have assumed that B is small enough that H_1 may be treated as a perturbation. If B is much stronger, the spin-orbit term becomes a perturbation relative to this Zeemann term.

$$H' = H_0 + H_1, \tag{18.2.87}$$

$$H_0 \equiv \frac{\vec{p}^2}{2m_e} + V \tag{18.2.88}$$

$$H_1 \equiv -\frac{e}{2m_e}\vec{B} \cdot (\vec{L} + g\vec{S}). \tag{18.2.89}$$

In this situation, we may use the basis $\left| n; \ell\ m_\ell, \frac{1}{2}\ m_s \right\rangle$ and compute

$$\delta_1 E = \left\langle n; \ell\ m_\ell, \frac{1}{2}\ m_s \left| H_1 \right| n; \ell\ m_\ell, \frac{1}{2}\ m_s \right\rangle \tag{18.2.90}$$

$$= -\frac{eB}{2m_e}\left(m_\ell + g m_s\right). \tag{18.2.91}$$

18.2.4 van der Waals Forces between atoms

[21]Consider two neutral atoms, which we shall label as atom 1 and atom 2. In this section, we will use perturbation theory to compute the expectation value of the energy due to their interactions.

The Coulomb potential between all the charges involved, can be split into 3 terms: the potential between the charges within atom 1, which we will dub V_1; the potential between the charges within atom 2, V_2; as well as the inter-atom potential,

$$V_{\text{int}} = \frac{1}{2}\sum_{\substack{e_a \in \text{A1} \\ e_b \in \text{A2}}} \sum_{\substack{\vec{x}_a \in \text{A1} \\ \vec{y}_b \in \text{A2}}} \frac{e_a e_b}{|\vec{x}_a - \vec{y}_b - \vec{R}|}. \tag{18.2.92}$$

Here, $\vec{x}_a$ points from the center-of-mass of atom 1 to its ath charge; whereas $\vec{y}_b$ points from the center-of-mass of atom 2 to its bth charge; and, finally, $\vec{R}$ points from the center-of-mass of atom

[21]The discussion here follows Weinberg. It is rather heavy-going; so look at the discussion in Sakurai first, if you desire a more friendly warm-up first.

1 to that of atom 2. Hence, $\vec{R}+\vec{y}_b$ points from the COM of A1 to the b charge; and therefore $\vec{x}_a-\vec{y}_b-\vec{R}$ is the vector from a to b.

The total Hamiltonian, ignoring spin effects, is then

$$H = H_0^{(\mathrm{A1})} + H_0^{(\mathrm{A2})} + H_1, \tag{18.2.93}$$

$$H_0^{(\mathrm{A1})} \equiv \sum_{e_a\in \mathrm{A1}} \frac{\vec{p}_a^{\,2}}{2m_a} + V_1, \qquad H_0^{(\mathrm{A2})} \equiv \sum_{e_b\in \mathrm{A2}} \frac{\vec{p}_b^{\,2}}{2m_b} + V_2, \tag{18.2.94}$$

$$H_1 \equiv V_{\mathrm{int}} = \frac{1}{2}\sum_{\substack{e_a\in \mathrm{A1}\\ e_b\in \mathrm{A2}}}\sum_{\substack{\vec{x}_a\in \mathrm{A1}\\ \vec{y}_b\in \mathrm{A2}}} \frac{e_a e_b}{|\vec{x}_a-\vec{y}_b-\vec{R}|}. \tag{18.2.95}$$

We will assume that $|\vec{x}_a|, |\vec{y}_b| \ll R$, i.e., the characteristic size of the atoms is much smaller than their separation; and there is negligible overlap between the wavefunctions of the charges in atom 1 with those in atom 2. These assumptions allow us to expand the H_1 as follows.

$$H_1 = \frac{1}{2}\sum_{\substack{e_a\in \mathrm{A1}\\ e_b\in \mathrm{A2}}}\sum_{\substack{\vec{x}_a\in \mathrm{A1}\\ \vec{y}_b\in \mathrm{A2}}}\sum_{\ell_a=0}^{\infty}\sum_{\ell_b=0}^{\infty} \frac{\left(-\vec{x}_a\cdot\vec{\nabla}_{\vec{R}}\right)^{\ell_a}}{\ell_a!}\frac{\left(\vec{y}_b\cdot\vec{\nabla}_{\vec{R}}\right)^{\ell_b}}{\ell_b!}\frac{e_a e_b}{|\vec{R}|} \tag{18.2.96}$$

Now, the $1/|\vec{x}_a-\vec{y}_a-\vec{R}|$ satisfies

$$\vec{\nabla}^2_{\vec{x}_a}\frac{1}{4\pi|\vec{x}_a-\vec{y}_b-\vec{R}|} = -\delta^{(3)}\left(\vec{x}_a-\vec{y}_a-\vec{R}\right) \tag{18.2.97}$$

$$\vec{\nabla}^2_{\vec{y}_b}\frac{1}{4\pi|\vec{x}_a-\vec{y}_b-\vec{R}|} = -\delta^{(3)}\left(\vec{x}_a-\vec{y}_a-\vec{R}\right); \tag{18.2.98}$$

whose right hand sides become zero for the limits $|\vec{x}_a|, |\vec{y}_b| \ll R$. This means H_1 satisfies the homogeneous Laplace equation with respect to $\vec{x}_a$, $\vec{y}_b$, and $\vec{R}$. In eq. (18.2.96), since $\vec{x}_a$ now occurs only within the power $(-\vec{x}_a\cdot\vec{\nabla})^{\ell_a}$ and $\vec{y}_b$ only within the $(\vec{y}_b\cdot\vec{\nabla})^{\ell_b}$; it must be that each term within the summation is proportional to

$$|\vec{x}_a|^{\ell_a} Y_{\ell_a}^{m_a}(\widehat{x}_a)|\vec{y}_b|^{\ell_b} Y_{\ell_b}^{m_b}(\widehat{y}_b) \equiv Y_{\ell_a}^{m_a}(\vec{x}_a) Y_{\ell_b}^{m_b}(\vec{y}_b), \tag{18.2.99}$$

because both $Y_{\ell_a}^{m_a}(\vec{x}_a)$ and $Y_{\ell_b}^{m_b}(\vec{y}_b)$ are homogeneous solutions of the Laplace equation with respect to $\vec{x}_a$ and $\vec{y}_b$. By dimensional analysis, the remaining factor must scale as $1/|\vec{R}|^{\ell_a+\ell_b+1}$. Moreover, the product of the spin$-\ell_a$ and spin$-\ell_b$ from the $Y_{\ell_a}^{m_a}(\vec{x}_a)$ and $Y_{\ell_b}^{m_b}(\vec{y}_b)$ must be compensated by a $Y_L^{-M}(\widehat{R})$ such that the result has zero spin, since H_1 itself is a scalar. That is: $|\ell_a-\ell_b| \le L \le \ell_a+\ell_b$ and $M=-(m_a+m_b)$. Altogether,

$$H_1 = \frac{1}{2}\sum_{\substack{e_a\in \mathrm{A1}\\ e_b\in \mathrm{A2}}}\sum_{\substack{\vec{x}_a\in \mathrm{A1}\\ \vec{y}_b\in \mathrm{A2}}}\sum_{\ell_a=0}^{\infty}\sum_{\ell_b=0}^{\infty} \frac{e_a e_b}{|\vec{R}|^{\ell_a+\ell_b+1}} \sum_{|\ell_a-\ell_b|\le L\le \ell_a+\ell_b} \chi_{\ell_a,\ell_b,L} \sum_{M=-L}^{+L} (-)^M Y_L^{-M}(\widehat{R})$$
$$\times \sum_{m_a+m_b=M} Y_{\ell_a}^{m_a}(\vec{x}_a) Y_{\ell_b}^{m_b}(\vec{y}_b)\, \langle \ell_a\ m_a, \ell_b\ m_b |\, L\ M; \ell_a\ \ell_b\rangle\,. \tag{18.2.100}$$

The second line amounts to 'adding' spin$-\ell_a$ to spin$-\ell_b$ to get a total spin L; i.e., it is proportional to Y_L^M. Then, we see that $\sum_M (-)^M Y_L^{-M} Y_L^M$ yields a spin 0 object. We may check this expression by recalling the spherical harmonic expansion, for $|\vec{R}| > |\vec{r}|$,

$$\frac{1}{|\vec{R}-\vec{r}|} = 4\pi \sum_{\ell=0}^{+\infty} \frac{1}{|\vec{R}|^{\ell+1}} \frac{1}{2\ell+1} \sum_{m=-\ell}^{+\ell} (-)^m Y_\ell^m(\vec{r}) Y_\ell^{-m}(\widehat{R}). \tag{18.2.101}$$

(Recall: $\overline{Y_\ell^m} = (-)^m Y_\ell^{-m}$.) For instance, setting $\vec{y}_b = \vec{0}$, we may identity $\vec{x}_a \leftrightarrow \vec{r}$. Then only the $\ell_b = 0 = m_b$ terms survive in eq. (18.2.100).

$$\sum_{e_a \in \mathrm{A1}} \sum_{\vec{x}_a \in \mathrm{A1}} \sum_{\ell_a=0}^{\infty} \frac{e_a e_b}{|\vec{R}|^{\ell_a+1}} \chi_{\ell_a,\ell_b=0,L=\ell_a} \sum_{m_a=-\ell_a}^{\ell_a} (-)^{m_a} Y_{\ell_a}^{-m_a}(\widehat{R}) Y_{\ell_a}^{m_a}(\vec{x}_a). \tag{18.2.102}$$

Let us define the electric multipole moments

$$E_{\ell_a}^{m_a}[1] \equiv \sum_{e_a \in \mathrm{A1}} \sum_{\vec{x}_a \in \mathrm{A1}} e_a Y_{\ell_a}^{m_a}(\vec{x}_a) \tag{18.2.103}$$

$$E_{\ell_b}^{m_b}[2] \equiv \sum_{e_b \in \mathrm{A2}} \sum_{\vec{y}_b \in \mathrm{A2}} e_b Y_{\ell_b}^{m_b}(\vec{y}_b). \tag{18.2.104}$$

Note that, when either $\ell_a = 0$ or $\ell_b = 0$,

$$E_0^0[1] = \sum_{e_a \in \mathrm{A1}} \sum_{\vec{x}_a \in \mathrm{A1}} e_a/\sqrt{4\pi} = 0 \tag{18.2.105}$$

$$\text{or} \qquad E_0^0[2] = \sum_{e_b \in \mathrm{A2}} \sum_{\vec{y}_b \in \mathrm{A2}} e_b/\sqrt{4\pi} = 0. \tag{18.2.106}$$

This is a consequence of the assumption that these atoms are neutral. Moreover, the $L = 0$ term must be zero because its coefficient must be gotten from multiplying H_1 by $Y_0^0(\widehat{R}) = 1/\sqrt{4\pi}$ and integrating with respect to $\widehat{R}$ over the 2−sphere.

$$L = 0: \qquad \frac{1}{2\sqrt{4\pi}} \sum_{\substack{e_a \in \mathrm{A1} \\ e_b \in \mathrm{A2}}} \sum_{\substack{\vec{x}_a \in \mathrm{A1} \\ \vec{y}_b \in \mathrm{A2}}} e_a e_b \int_{\mathbb{S}^2} \frac{\mathrm{d}^2\widehat{R}}{|\vec{x}_a - \vec{y}_b - \vec{R}|} \tag{18.2.107}$$

Now,

$$\int_{\mathbb{S}^2} \frac{\mathrm{d}^2\widehat{R}}{|\vec{r}-\vec{R}|} = \int_{\mathbb{S}^2} \mathrm{d}^2\widehat{R} \left| r^2 + R^2 - rR\widehat{R}\cdot\widehat{r} \right|^{-1/2} \tag{18.2.108}$$

$$= 2\pi \int_{-1}^{+1} \mathrm{d}c \left| r^2 + R^2 - rRc \right|^{-1/2} \tag{18.2.109}$$

$$= -\frac{2\pi}{Rr} \left(|r-R| - |r+R| \right) \overset{R>r}{\to} \frac{4\pi}{R}. \tag{18.2.110}$$

Hence,

$$L=0: \qquad \frac{1}{2\sqrt{4\pi}}\sum_{\substack{e_a\in \mathrm{A1}\\ e_b\in \mathrm{A2}}}\sum_{\substack{\vec{x}_a\in \mathrm{A1}\\ \vec{y}_b\in \mathrm{A2}}} e_a e_b \int_{\mathbb{S}^2}\frac{\mathrm{d}^2\widehat{R}}{|\vec{x}_a-\vec{y}_b-\vec{R}|}=\frac{\sqrt{4\pi}}{2}\sum_{\substack{e_a\in \mathrm{A1}\\ e_b\in \mathrm{A2}}}\sum_{\substack{\vec{x}_a\in \mathrm{A1}\\ \vec{y}_b\in \mathrm{A2}}}\frac{e_a e_b}{|\vec{R}|}=0; \tag{18.2.111}$$

again by neutrality.

Finally, consider the simultaneous parity operations $\vec{x}_a\to-\vec{x}_a$, $\vec{y}_b\to-\vec{y}_b$ and $\vec{R}\to-\vec{R}$; which leaves $H_1\propto 1/|\vec{x}_a-\vec{y}_b-\vec{R}|$ invariant. But $Y_\ell^m(-\widehat{n})=(-)^\ell Y_\ell^m(\widehat{n})$. Examining eq. (18.2.100), we see that

$$Y_L^{-M}(-\widehat{R})Y_{\ell_a}^{m_a}(-\vec{x}_a)Y_{\ell_b}^{m_b}(-\vec{y}_b)=(-)^{\ell_a+\ell_b+L}Y_L^{-M}(\widehat{R})Y_{\ell_a}^{m_a}(\vec{x}_a)Y_{\ell_b}^{m_b}(\vec{y}_b). \tag{18.2.112}$$

But since such a parity operation must leave the H_1 invariant, and since the spherical harmonics are linearly independent basis functions, $\ell_a+\ell_b+L$ must be even.

Taking all these considerations into account, we may surmise eq. (18.2.100) reads

$$\begin{aligned}H_1=\frac{1}{2}\sum_{\ell_a=1}^{\infty}\sum_{\ell_b=1}^{\infty}\frac{1}{|\vec{R}|^{\ell_a+\ell_b+1}}\sum_{\substack{|\ell_a-\ell_b|\le L\le \ell_a+\ell_b\\ L\neq 0\\ \ell_a+\ell_b+L\text{ even}}}\chi_{\ell_a,\ell_b,L}\sum_{M=-L}^{+L}(-)^M Y_L^{-M}(\widehat{R})\\ \times\sum_{m_a+m_b=M}E_{\ell_a}^{m_a}[1]E_{\ell_b}^{m_b}[2]\,\langle \ell_a\ m_a,\ell_b\ m_b|\,L\ M;\ell_a\ \ell_b\rangle\,.\end{aligned} \tag{18.2.113}$$

To zeroth order, $H_1=0$ and the eigenstates of H_0 are the tensor product of the eigenstate of atom 1 with those of atom 2 – namely $|E_1\rangle\otimes|E_2\rangle$ – which obeys

$$H_0^{(\mathrm{A1})}|E_1\rangle=E_1|E_1\rangle \qquad \text{and} \qquad H_0^{(\mathrm{A1})}|E_2\rangle=E_2|E_2\rangle\,. \tag{18.2.114}$$

At first order in perturbation theory, the corrections to the energies are

$$\begin{aligned}\delta_1(E_1|E_2)=\frac{1}{2}\sum_{\ell_a=1}^{\infty}\sum_{\ell_b=1}^{\infty}\frac{1}{|\vec{R}|^{\ell_a+\ell_b+1}}\sum_{\substack{|\ell_a-\ell_b|\le L\le \ell_a+\ell_b\\ L\neq 0\\ \ell_a+\ell_b+L\text{ even}}}\chi_{\ell_a,\ell_b,L}\sum_{M=-L}^{+L}(-)^M Y_L^{-M}(\widehat{R})\\ \times\sum_{m_a+m_b=M}\left\langle E_1\left|E_{\ell_a}^{m_a}[1]\right|E_1\right\rangle\left\langle E_2\left|E_{\ell_b}^{m_b}[2]\right|E_2\right\rangle\,\langle \ell_a\ m_a,\ell_b\ m_b|\,L\ M;\ell_a\ \ell_b\rangle\,.\end{aligned} \tag{18.2.115}$$

This $\delta_1(E_1|E_2)$ may be interpreted as the potential energy due to the interactions between atoms 1 and 2.

Under parity, we have just noted that the electric multipole operators transform as $E_\ell^m\to(-)^\ell E_\ell^m$. Hence, if the dynamics of the individual atomic systems is parity invariant – their Hamiltonians commute with the parity operator $[H_0^{(\mathrm{A1})},P]=0=[H_0^{(\mathrm{A2})},P]$ – then the expectation value $\langle E_\ell^m\rangle$ is zero unless ℓ is even because

$$P|E_{1,2}\rangle=\pm|E_{1,2}\rangle \tag{18.2.116}$$

$$\Rightarrow\langle E_{1,2}|PE_\ell^m P|\,E_{1,2}\rangle=(\langle E_{1,2}|\,P)\,E_\ell^m\,(P\,|E_{1,2}\rangle)=\langle E_{1,2}|E_\ell^m|\,E_{1,2}\rangle \tag{18.2.117}$$

$$=\langle E_{1,2}|(PE_\ell^m P)|\,E_{1,2}\rangle=(-)^\ell\langle E_{1,2}|E_\ell^m|\,E_{1,2}\rangle\,. \tag{18.2.118}$$

To sum:

To leading order, the potential energy arising from the interactions between neutral atoms, whose individual dynamics obeys parity, vanishes unless their electric multipole moments are even.

$$\delta_1(E_1|E_2) = \frac{1}{2}\sum_{\substack{\ell_a=2\\ \ell_a \text{ even}}}^{\infty}\sum_{\substack{\ell_b=1\\ \ell_b \text{ even}}}^{\infty}\frac{1}{|\vec{R}|^{\ell_a+\ell_b+1}}\sum_{\substack{|\ell_a-\ell_b|\le L\le \ell_a+\ell_b\\ L\neq 0\\ \ell_a+\ell_b+L \text{ even}}}\chi_{\ell_a,\ell_b,L}\sum_{M=-L}^{+L}(-)^M Y_L^{-M}(\widehat{R})$$
$$\times\sum_{m_a+m_b=M}\left\langle E_1\left|E_{\ell_a}^{m_a}[1]\right|E_1\right\rangle\left\langle E_2\left|E_{\ell_b}^{m_b}[2]\right|E_2\right\rangle\langle \ell_a\ m_a,\ell_b\ m_b|\,L\ M;\ell_a\ \ell_b\rangle\,. \tag{18.2.119}$$

Problem 18.4. Work out eq. (18.2.119) up to the quadrupole order, i.e., $0 \le \ell_a, \ell_b \le 2$, in terms of the electric dipole

$$\vec{D}_{(1)} \equiv \sum_{a\in \mathrm{A1}} e_a \vec{X}_a \tag{18.2.120}$$
$$\vec{D}_{(2)} \equiv \sum_{b\in \mathrm{A2}} e_b \vec{Y}_b; \tag{18.2.121}$$

and traceless quadrupole

$$Q^{ij}_{(1)} \equiv \sum_{a\in \mathrm{A1}} e_a\left(X_a^i X_a^j - \frac{1}{3}\delta^{ij}\vec{X}_a^2\right) \tag{18.2.122}$$
$$Q^{ij}_{(2)} \equiv \sum_{b\in \mathrm{A2}} e_b\left(Y_a^i Y_a^j - \frac{1}{3}\delta^{ij}\vec{Y}_a^2\right) \tag{18.2.123}$$

operators. Hint: Remember the expansion in eq. (18.2.96). □

Unpolarized Atoms If the atomic states $|E; j', m'\rangle$ are equally likely to take on any azimuthal m' value for a fixed j', we say they are unpolarized. In such a case, we will average over m', and invoke Wigner-Eckart to see that $m = 0$ on the E_ℓ^m in order to produce a non-zero result.

$$\langle\langle E_\ell^m\rangle\rangle \equiv \frac{1}{2j'+1}\sum_{m'=-j'}^{+j'}\langle j', m'\,|E_\ell^m|\,j', m'\rangle \tag{18.2.124}$$
$$= \frac{\langle j'||E_\ell||j'\rangle}{2j'+1}\delta^0_m\sum_{m'=-j'}^{+j'}\langle j'\ m';\ell\ j'|\,\ell\ 0, j'\ m'\rangle\,. \tag{18.2.125}$$

Weinberg shows in the discussion leading up to his eq. (4.3.41) and the one leading up to (4.4.21), that $\sum_{m'}\langle j'\ m';\ell\ j'|\,\ell\ 0, j'\ m'\rangle$ is zero unless $\ell = 0$. Since neither ℓ_a nor ℓ_b can be zero in our case, this tells us:

To first order in perturbation theory, a pair of unpolarized atoms suffers no shift in energies due to their mutual interactions.

That teaches us, to study the effective potential energy between two unpolarized atoms, we have to go to second order in perturbation theory.

$$\delta_2(E_1|E_2) = \sum_{E_1',E_2'} \frac{|\langle E_1' \otimes E_2' | H_1 | E_1 \otimes E_2 \rangle|^2}{E_1 + E_2 - E_1' - E_2'} \tag{18.2.126}$$

The dominant term, as $R \to \infty$, arises from multiplying the lowest power of $1/R$ in eq. (18.2.113). We observe that

$$\langle j'\ m' | E_\ell^m | j''\ m'' \rangle \propto \langle j'\ m'; \ell\ j'' | \ell\ m, j''\ m'' \rangle \tag{18.2.127}$$

is generically non-zero starting from $j' = 0$ – this simply requires $\ell = j''$, for instance. The electric dipole, as Weinberg reminds us, would induce a transition from $1s$ to $2p$. To lowest order in $1/R$, we take the $\ell_a = 1 = \ell_b$ term in eq. (18.2.113),

$$\delta_2(E_1|E_2) \approx \frac{1}{4R^6} \sum_{E_1'+E_2' \neq E_1+E_2} (E_1 + E_2 - E_1' - E_2')^{-1} \left| \chi_{1,1,L=2} \sum_{M=-2}^{+2} (-)^M Y_2^{-M}(\widehat{R}) \right.$$
$$\left. \times \sum_{m_a+m_b=M} \langle E_1' | E_1^{m_a}[1] | E_1 \rangle \langle E_2' | E_1^{m_b}[2] | E_2 \rangle \langle 1\ m_a, 1\ m_b | 2\ M; 1\ 1 \rangle \right|^2 . \tag{18.2.128}$$

Unpolarized Ground States Attract If E_1 and E_2 are the ground states of the individual atoms 1 and 2; we see that the van der Waals effective potential not only goes as $1/R^6$, it is in fact *attractive*, because the potential energy is negative, since $E_1 + E_2 - E_1' - E_2' < 0$.

18.3 Magnetic Moment

Interaction of electron with $\vec{B}$ field

$$-\vec{\mu} \cdot \vec{B} \in H_{\rm I} \tag{18.3.1}$$
$$\vec{\mu} \equiv g \frac{e}{2m} \vec{S}. \tag{18.3.2}$$

$g - 2 =$

19 JWKB (Short Wavelength) Approximation

When the wavefunction ψ varies much more rapidly than the potential V, it is possible to obtain an approximate solution to the Schrödinger equation up to quadrature (i.e., in terms of explicit integrals). In fact, this JWKB – more often simply dubbed WKB – scheme finds widespread application beyond QM: geometric and wave optics, wave solutions in curved spacetimes, etc.

3 Dimensions We begin with the ansatz (given in Sakurai), for real ρ and S,

$$\psi(t,\vec{x}) = \sqrt{\rho(t,\vec{x})}\exp\left(\frac{i}{\hbar}S(t,\vec{x})\right) \tag{19.0.1}$$

where we have restored $\hbar$. The key assumption we shall make is that *derivatives on S are to be regarded as being more dominant than derivatives on ρ*; that is, the phase $\exp(iS/\hbar)$ oscillates rapidly whereas the amplitude $\sqrt{\rho}$ varies slowly. Now, the Schrödinger equation reads

$$i\hbar\partial_t\psi = \left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V\right)\psi. \tag{19.0.2}$$

That means at leading order in derivatives, we have

$$i\hbar\partial_t\psi \approx \sqrt{\rho}i^2\partial_t S e^{iS/\hbar} \tag{19.0.3}$$

$$\begin{aligned} -\hbar^2\vec{\nabla}^2\psi &\approx -\hbar^2\vec{\nabla}\cdot\left(\sqrt{\rho}\frac{i}{\hbar}\vec{\nabla}Se^{iS/\hbar}\right) \\ &\approx -\hbar^2\sqrt{\rho}\frac{i^2}{\hbar^2}\vec{\nabla}S\cdot\vec{\nabla}Se^{iS/\hbar}; \end{aligned} \tag{19.0.4}$$

so that Schrödinger's equation now becomes the following

$$\partial_t S + \frac{(\vec{\nabla}S)^2}{2m} + V = 0. \tag{19.0.5}$$

This is the Hamilton-Jacobi equation in classical mechanics.

Notice all the $\hbar$s have canceled out. Because each derivative comes with one power of $\hbar$, JWKB is sometimes called the semi-classical limit, in the sense that $\hbar$ can be considered 'small'. However, $\hbar$ is dimension-ful (namely, $[\hbar]$ is energy $\times$ time) and therefore cannot be 'small' or 'large'. Instead, what JWKB does it assumes the phase $e^{iS/\hbar}$ varies more rapidly than $\sqrt{\rho}$, and the $\hbar$s happen to count the number of derivatives. In any case, we see that if we first re-scale

$$\vec{y} \equiv \sqrt{2m}\vec{x}, \tag{19.0.6}$$

followed by identifying

$$\frac{\mathrm{d}\vec{y}(t)}{\mathrm{d}t} = \nabla_{\vec{y}}S; \tag{19.0.7}$$

then we have

$$\partial_t S(t,\vec{y}(t)) + \nabla_{\vec{y}}S\cdot\nabla_{\vec{y}}S = -V(\vec{y}) \tag{19.0.8}$$

$$\partial_t S(t,\vec{y}(t)) + \dot{\vec{y}}\cdot\nabla_{\vec{y}}S = -V \tag{19.0.9}$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -V \tag{19.0.10}$$

When V is independent of time, we may seek the stationary states; where $\psi \propto e^{-iEt}$. Thus,

$$S(t, \vec{x}) = W(\vec{x}) - E \cdot t; \tag{19.0.11}$$

and the Hamilton-Jacobi translates into

$$(\vec{\nabla} W)^2 = 2m(E - V). \tag{19.0.12}$$

By taking an additional gradient,

$$U^i \partial_i U^j = -m \partial_j V \tag{19.0.13}$$

$$U^i \equiv \partial_i W. \tag{19.0.14}$$

This 'fixed energy' JWKB approximation scheme has a relationship with the corresponding 'fixed energy' path integral; see Shankar for a discussion.

One Dimension We turn to one dimension, where – as we shall see shortly – in the short wavelength limit it is possible to obtain W by integration. However, we wish to do things more systematically. First, we will revert to setting $\hbar = 1$, re-writing the Schrödinger equation as

$$\epsilon^2 \psi'' + U\psi = 0, \qquad U \equiv 2m(E - V). \tag{19.0.15}$$

The ϵ is *not* $\hbar$, but a fictitious dimensionless parameter that counts derivatives; $1/\epsilon$ will turn out to be an integral, for e.g. We will then postulate the following JWKB ansatz:

$$\psi(x) = \sum_{\ell=0}^{\infty} \epsilon^\ell \alpha_\ell(x) e^{iS(x)/\epsilon}. \tag{19.0.16}$$

Plugging this into our ODE, we obtain

$$0 = \sum_{\ell=0}^{\infty} \epsilon^\ell \left(\alpha_\ell(x) \left(S'(x)^2 - U(x) \right) - i \left(\alpha_{\ell-1}(x) S''(x) + 2S'(x)\alpha'_{\ell-1}(x) \right) - \alpha''_{\ell-2}(x) \right) \tag{19.0.17}$$

with the understanding that $\alpha_{-2}(x) = \alpha_{-1}(x) = 0$. We need to set the coefficients of ϵ^ℓ to zero. The first two terms ($\ell = 0, 1$) give us solutions to $S(x)$ and $\alpha_0(x)$.

$$0 = \alpha_0 \left(S'(x)^2 - U(x) \right) \qquad \Rightarrow \qquad S_\pm(x) = \sigma_0 \pm \int^x \mathrm{d}x' \sqrt{U(x')}; \ \sigma_0 = \text{const.}$$

$$0 = -i\epsilon \left(2\alpha'_0(x) S'(x) + \alpha_0(x) S''(x) \right) \qquad \Rightarrow \qquad \alpha_0(x) = \frac{C_0}{U(x)^{1/4}}$$

(While the solutions $S_\pm(x)$ contains two possible signs, the $\pm$ in S' and S'' factors out of the second equation and thus α_0 does not have two possible signs.)

Problem 19.1. Recursion relation for higher order terms By considering the $\ell \geq 2$ terms in eq. (19.0.17), show that there is a recursion relation between $\alpha_\ell(x)$ and $\alpha_{\ell+1}(x)$. Can

you use them to deduce the following two linearly independent JWKB solutions?

$$0 = \epsilon^2 \psi_\pm''(x) + U(x)\psi_\pm(x) \tag{19.0.18}$$

$$\psi_\pm(x) = \frac{1}{U(x)^{1/4}} \exp\left[\mp \frac{i}{\epsilon}\int^x \mathrm{d}x' \sqrt{U(x')}\right] \sum_{\ell=0}^{\infty} \epsilon^\ell Q_{(\ell|\pm)}(x), \tag{19.0.19}$$

$$Q_{(\ell|\pm)}(x) = \pm\frac{1}{2}\int^x \frac{\mathrm{d}x'}{U(x')^{1/4}} \frac{\mathrm{d}^2}{\mathrm{d}x'^2}\left(\frac{Q_{(\ell-1|\pm)}(x')}{U(x')^{1/4}}\right), \qquad Q_{(0|\pm)}(x) \equiv 1 \tag{19.0.20}$$

To lowest order

$$\psi_\pm(x) = \frac{1}{U^{1/4}(x)} \exp\left[\mp \frac{i}{\epsilon}\int^x \mathrm{d}x' \sqrt{U[x']}\right] (1 + \mathcal{O}[\epsilon])\,. \tag{19.0.21}$$

Note: in these solutions, the $\sqrt{\cdot}$ and $\sqrt[4]{\cdot}$ are positive roots. □

JWKB Counts Derivatives In terms of the $Q_{(n)}$s we see that the JWKB method is really an approximation that works whenever each derivative $\mathrm{d}/\mathrm{d}x$ acting on some power of $U(x)$ yields a smaller quantity, i.e., roughly speaking $\mathrm{d}\ln U(x)/\mathrm{d}x \sim \epsilon \ll 1$; this small derivative approximation is related to the short wavelength approximation. Also notice from the exponential $\exp[iS/\epsilon] \sim \exp[\pm(i/\epsilon)\int\sqrt{U}]$ that the $1/\epsilon$ indicates an integral (namely, an inverse derivative). To sum:

> The ficticious parameter $\epsilon \ll 1$ in the JWKB solution of $\epsilon^2\psi'' + U\psi = 0$ counts the number of derivatives; whereas $1/\epsilon$ is an integral. The JWKB approximation works well whenever each additional derivative acting on some power of U yields a smaller and smaller quantity.

Turning Points & Connection Formulas Whenever $E > V$, we expect an oscillatory eigensolution; while whenever $E < V$, we expect a damped one.

$$\psi(x) \approx \frac{1}{\sqrt[4]{U}}\left(C_+ e^{\frac{i}{\epsilon}\int^x \sqrt{U}\mathrm{d}x} + C_- e^{-\frac{i}{\epsilon}\int^x \sqrt{U}\mathrm{d}x}\right), \qquad E > V \Rightarrow U > 0 \tag{19.0.22}$$

$$\approx \frac{1}{\sqrt[4]{-U}}\left(C'_+ e^{\frac{1}{\epsilon}\int^x \sqrt{-U}\mathrm{d}x} + C'_- e^{-\frac{1}{\epsilon}\int^x \sqrt{-U}\mathrm{d}x}\right), \qquad E < V \Rightarrow -U > 0. \tag{19.0.23}$$

What happens when $E \approx V$? Notice the denominator in the $1/\sqrt[4]{U}$ of the JWKB solution goes to zero there, and the approximation is likely breaking down. The strategy is then as follows. Suppose at $x = x_\star$, we have $E = V(x_\star)$, then we may Taylor expand

$$U(x) = 2m(E - V(x)) = 2m(E - V(x_\star) - (x - x_\star)V'(x_\star) + \dots) \tag{19.0.24}$$

$$= -2m(x - x_\star)V'(x_\star) + \mathcal{O}\left((x - x_\star)^2\right). \tag{19.0.25}$$

Since coordinates are arbitrary, let us re-center our 1D system such that $z \equiv (x - x_\star)$.

$$\psi''(z) - 2mV'(x_\star)z\psi(z) = 0 \tag{19.0.26}$$

The solution to $\psi'' - \lambda z \psi = 0$ for constant λ are the Airy functions $\mathrm{Ai}[\lambda^{\frac{1}{3}} z]$ and $\mathrm{Bi}[\lambda^{\frac{1}{3}} z]$, which in turn are related to Bessel functions. Therefore, to leading order, near $x \approx x_\star$,

$$\psi(x) \approx C_A \mathrm{Ai}[\sqrt[3]{2mV'(x_\star)}(x - x_\star)] + C_B \mathrm{Bi}[\sqrt[3]{2mV'(x_\star)}(x - x_\star)]. \tag{19.0.27}$$

We will now take their large argument limits so as to join these solutions to the JWKB ones. In particular, let us record

$$\mathrm{Ai}(z \to \infty) \sim \frac{\exp\left(-\frac{2}{3} z^{\frac{3}{2}}\right)}{2\sqrt{\pi} z^{1/4}} \left(1 + \mathcal{O}(z^{-3/2})\right), \tag{19.0.28}$$

$$\mathrm{Bi}(z \to \infty) \sim \frac{\exp\left(+\frac{2}{3} z^{\frac{3}{2}}\right)}{\sqrt{\pi} z^{1/4}} \left(1 + \mathcal{O}(z^{-3/2})\right). \tag{19.0.29}$$

and

$$\begin{aligned} &\mathrm{Ai}(z \to -\infty) \qquad (19.0.30)\\ &\sim \frac{1}{\sqrt{\pi}(-z)^{1/4}} \left(\cos\left(\frac{2}{3}(-z)^{\frac{3}{2}} - \frac{\pi}{4}\right) \left(1 + \mathcal{O}((-z)^{-3})\right) + \sin\left(\frac{2}{3}(-z)^{\frac{3}{2}} - \frac{\pi}{4}\right) \mathcal{O}((-z)^{-3/2}) \right), \\ &\mathrm{Bi}(z \to -\infty) \qquad (19.0.31)\\ &\sim \frac{1}{\sqrt{\pi}(-z)^{1/4}} \left(-\sin\left(\frac{2}{3}(-z)^{\frac{3}{2}} - \frac{\pi}{4}\right) \left(1 + \mathcal{O}((-z)^{-3})\right) + \cos\left(\frac{2}{3}(-z)^{\frac{3}{2}} - \frac{\pi}{4}\right) \mathcal{O}((-z)^{-3/2}) \right). \end{aligned}$$

Case 1: Confining Potential Let us first examine the case where $V(x \to \pm\infty) \to \infty$, where the potential is strictly confining. For simplicity we will assume $E > V$ for a single region of space $x_1 < x < x_2$. In such a situation we know that the wavefunction must necessarily decay for $x < x_1$ and $x > x_2$; so

$$\psi(x \sim x_1) \approx C_A \mathrm{Ai}[\sqrt[3]{2m|V'(x_1)|}(x_1 - x)] \tag{19.0.32}$$

$$\psi(x \lessapprox x_1) \sim C_A \frac{\exp\left(-\frac{2}{3}\sqrt{2m|V'(x_1)|}(x_1 - x)^{\frac{3}{2}}\right)}{2\sqrt{\pi}(2m|V'(x_1)|)^{\frac{1}{12}}(x_1 - x)^{\frac{1}{4}}} \tag{19.0.33}$$

$$\psi(x \gtrapprox x_1) \sim C_A \frac{\cos\left(\frac{2}{3}\sqrt{2m|V'(x_1)|}(x - x_1)^{\frac{3}{2}} - \frac{\pi}{4}\right)}{\sqrt{\pi}(2m|V'(x_1)|)^{\frac{1}{12}}(x - x_1)^{1/4}} \tag{19.0.34}$$

and

$$\psi(x \sim x_2) \approx C'_A \mathrm{Ai}[\sqrt[3]{2m|V'(x_2)|}(x - x_2)] \tag{19.0.35}$$

$$\psi(x \lessapprox x_2) \sim C'_A \frac{\cos\left(\frac{2}{3}\sqrt{2m|V'(x_2)|}(x_2 - x)^{\frac{3}{2}} - \frac{\pi}{4}\right)}{\sqrt{\pi}(2m|V'(x_2)|)^{\frac{1}{12}}(x - x_2)^{1/4}} \tag{19.0.36}$$

$$\psi(x \gtrapprox x_2) \sim C'_A \frac{\exp\left(-\frac{2}{3}\sqrt{2m|V'(x_2)|}(x - x_2)^{\frac{3}{2}}\right)}{2\sqrt{\pi}(2m|V'(x_2)|)^{\frac{1}{12}}(x - x_2)^{\frac{1}{4}}}. \tag{19.0.37}$$

On the other hand, the JWKB solution can be superposed to yield cosine. Remember $U = 2m(E-V)$; if we start integrating from x_1, we may express the solution as

$$\psi_{\text{JWKB}}(x_1 < x < x_2) \approx \chi_A \frac{\cos\left(\int_{x_1}^{x} \sqrt{2m(E-V(x'))}\mathrm{d}x' - \frac{\pi}{4}\right)}{\sqrt{\pi}\sqrt[4]{2m(E-V(x))}}. \tag{19.0.38}$$

This guarantees that, near the left turning point $x \sim x_1$, we may match unto the Airy solution.

$$\psi_{\text{JWKB}}(x \to x_1) \approx \chi_A \frac{\cos\left(\frac{2}{3}\sqrt{2m|V'(x_1)|}(x-x_1)^{\frac{3}{2}} - \frac{\pi}{4}\right)}{\sqrt{\pi}\sqrt[4]{2mV'(x_1)(x-x_1)}} \tag{19.0.39}$$

$$\frac{C_A}{\sqrt{\pi}(2m|V'(x_1)|)^{\frac{1}{12}}} = \frac{\chi_A}{\sqrt{\pi}\sqrt[4]{2mV'(x_1)}} \tag{19.0.40}$$

Near the right turning point,

$$\begin{aligned}
&\psi_{\text{JWKB}}(x \to x_2) \\
&\approx \chi_A \frac{\cos\left(\left(\int_{x_1}^{x_2} - \int_{x}^{x_2}\right)\mathrm{d}x'\sqrt{2m(E-V(x'))} - \frac{\pi}{4}\right)}{\sqrt{\pi}\sqrt[4]{2m(E-V(x))}} &(19.0.41)\\
&\approx \chi_A \frac{\cos\left(\int_{x_1}^{x_2}\sqrt{2m(E-V(x'))}\mathrm{d}x' - \frac{\pi}{2} - \frac{2}{3}\sqrt{2mV'(x_2)(x_2-x)} + \frac{\pi}{4}\right)}{\sqrt{\pi}\sqrt[4]{2mV'(x_2)\cdot(x_2-x)}} &(19.0.42)
\end{aligned}$$

We now demand that this be matched unto the Airy function solution near $x \sim x_2$. We have already fixed χ_A in terms of C_A. We may demand that the integral from x_1 to x_2 yield the same cosine or its negative; namely

$$\psi_{\text{JWKB}}(x \to x_2) = \pm\chi_A \frac{\cos\left(\frac{2}{3}\sqrt{2mV'(x_2)(x_2-x)} - \frac{\pi}{4}\right)}{\sqrt{\pi}\sqrt[4]{2mV'(x_2)\cdot(x_2-x)}} \tag{19.0.43}$$

Then C'_A will be entirely fixed by χ_A and hence by C_A. This remaining constant C_A will in turn be fixed (up to a multiplicative phase factor) by the normalization $\int_{\mathbb{R}}|\psi|^2\mathrm{d}x = 1$. We therefore need to impose the following condition

$$\int_{x_1}^{x_2}\sqrt{2m(E-V(x'))}\mathrm{d}x' - \frac{\pi}{2} = n\pi, \qquad n = 0,1,2,3,\ldots \tag{19.0.44}$$

This allows the energy E to be determined.

Problem 19.2. Use JWKB to find the approximate energy eigenfunctions and levels of the Hamiltonian

$$H = \frac{P^2}{2m} + \lambda X^{2n}, \qquad \lambda > 0,\ n = 1,2,3,\ldots. \tag{19.0.45}$$

Try to obtain the energy levels for arbitrary n. If you can't, do it for the low lying ns. □

Case II: Tunneling

20 Density Matrices: Schrödinger Picture

Schrödinger picture In a statistical ensemble of quantum states $\{|\alpha_i\rangle\}$, with i being the enumeration label, the statistical average of the quantum expectation value of some operator A is given by

$$\langle\langle A\rangle\rangle \equiv \sum_i p_i \langle\alpha_i|A|\alpha_i\rangle ,$$

where p_i corresponds to the probability that a randomly picked system is $|\alpha_i\rangle$. (In particular, $\sum_i p_i = 1$; and, the sum over i does not necessarily equal to the dimensionality D_V of the vector space.) Now, let us define the density operator

$$\widehat{\rho} \equiv \sum_i p_i |\alpha_i\rangle\langle\alpha_i| .$$

Consider

$$\begin{aligned}\mathrm{Tr}\,[\widehat{\rho}\cdot A] &= \sum_{\ell=1}^{D_V}\sum_i p_i \langle\ell|\mathbb{I}|\alpha_i\rangle\langle\alpha_i|A|\ell\rangle \\ &= \sum_{\ell=1}^{D_V}\sum_i p_i \langle\alpha_i|A|\ell\rangle\langle\ell|\mathbb{I}|\alpha_i\rangle \\ &= \sum_i p_i \langle\alpha_i|A|\alpha_i\rangle = \langle\langle A\rangle\rangle.\end{aligned}$$

Therefore the density operator is a central object in computing the statistical average of the quantum expectation value of some operator A.

Time evolution How does this statistical ensemble evolve with time? In the Schrödinger picture, if the quantum state at some initial time t' is $|\alpha\rangle$, at the time $t > t'$ it has evolved to $U[t,t']|\alpha\rangle$, where if H denotes the Hamiltonian $i\partial_t U[t,t'] = H[t]U[t,t']$ and $U[t=t'] = \mathbb{I}$. Suppose, at time t', the density operator is

$$\widehat{\rho}_0 \equiv \sum_i p_i |\alpha_i\rangle\langle\alpha_i| .$$

At time $t > t'$, we have

$$\widehat{\rho}[t] = U[t,t']\widehat{\rho}_0 U[t,t']^\dagger.$$

Taking the time derivative gives us the equation for the density matrix itself.

$$i\partial_t\widehat{\rho}(t) = [H,\widehat{\rho}(t)] \tag{20.0.1}$$

By inserting complete sets of position eigenstates,

$$\begin{aligned}\mathrm{Tr}\,[\widehat{\rho}[t]\cdot A] &= \sum_{\vec{x},\vec{x}',\vec{y},\vec{y}'} \langle\vec{x}|U[t,t']|\vec{x}'\rangle\langle\vec{x}'|\widehat{\rho}_0|\vec{y}'\rangle\left\langle\vec{y}'\left|U[t,t']^\dagger\right|\vec{y}\right\rangle\langle\vec{y}|A|\vec{x}\rangle , \\ &= \sum_{\vec{x},\vec{x}',\vec{y},\vec{y}'} \langle\vec{x}|U[t,t']|\vec{x}'\rangle\langle\vec{x}'|\widehat{\rho}_0|\vec{y}'\rangle\langle\vec{y}|U[t,t']|\vec{y}'\rangle^\star\langle\vec{y}|A|\vec{x}\rangle .\end{aligned}$$

We have

$$\langle \vec{x}\,|U[t,t']|\,\vec{x}'\rangle = \int_{\vec{x}'}^{\vec{x}} \mathcal{D}\vec{q}\exp\left[i\int_{t'}^{t} L[\vec{q},\dot{\vec{q}}]\mathrm{d}\tau\right]$$
$$\langle \vec{y}\,|U[t,t']|\,\vec{y}'\rangle^{\star} = \int_{\vec{y}'}^{\vec{y}} \mathcal{D}\vec{q}'\exp\left[-i\int_{t'}^{t} L[\vec{q}',\dot{\vec{q}}']\mathrm{d}\tau'\right];$$

where we are assuming the path integral over the conjugate momentum can be performed to leave a Lagrangian that depends solely on the positions $\{\vec{q},\vec{q}'\}$ and velocities $\{\dot{\vec{q}},\dot{\vec{q}}'\}$.

$$\langle\langle A\rangle\rangle[t] = \int \mathrm{d}^D\vec{x}\int \mathrm{d}^D\vec{y} K_{\text{in-in}}\left[\vec{x},t;\vec{y},t'\right]\langle \vec{y}\,|A|\,\vec{x}\rangle;$$

with

$$\begin{aligned}
K_{\text{in-in}}[\vec{x},t;\vec{y},t'] &\equiv \frac{1}{i^N}\frac{\delta^N}{\delta J^+_{i_1}[t]\ldots\delta J^+_{i_N}[t]}\bigg|_{\vec{J}^+=\vec{J}^-=0}\int \mathrm{d}^D\vec{x}'\int \mathrm{d}^D\vec{y}'\int_{\vec{x}'}^{\vec{x}}\mathcal{D}\vec{q}_+\int_{\vec{y}'}^{\vec{y}}\mathcal{D}\vec{q}_-\widehat{\rho}[\vec{x}',\vec{y}'] \\
&\qquad\times\exp\left[i\int_{t'}^{t}\left(L[\vec{q}_+,\dot{\vec{q}}_+]-L[\vec{q}_-,\dot{\vec{q}}_-]+\vec{J}^+\cdot\vec{q}_+-\vec{J}^-\cdot\vec{q}_-\right)\mathrm{d}\tau\right] \\
&\equiv \frac{1}{(-i)^N}\,\frac{\delta^N}{\delta J^-_{i_1}[t]\ldots\delta J^-_{i_N}[t]}\bigg|_{\vec{J}^+=\vec{J}^-=0}\int \mathrm{d}^D\vec{x}'\int \mathrm{d}^D\vec{y}'\int_{\vec{x}'}^{\vec{x}}\mathcal{D}\vec{q}_+\int_{\vec{y}'}^{\vec{y}}\mathcal{D}\vec{q}_-\widehat{\rho}[\vec{x}',\vec{y}'] \\
&\qquad\times\exp\left[i\int_{t'}^{t}\left(L[\vec{q}_+,\dot{\vec{q}}_+]-L[\vec{q}_-,\dot{\vec{q}}_-]+\vec{J}^+\cdot\vec{q}_+-\vec{J}^-\cdot\vec{q}_-\right)\mathrm{d}\tau\right], \\
\widehat{\rho}[\vec{x}',\vec{y}'] &\equiv \langle\vec{x}'\,|\widehat{\rho}_0|\,\vec{y}'\rangle, \qquad\qquad \dot{\vec{q}}\equiv\partial_\tau\vec{q}.
\end{aligned}$$

Statistical ensemble of position correlations Let A be a product of position operators.

$$\begin{aligned}
\mathrm{Tr}\left[\widehat{\rho}[t]\cdot q^{i_1}\ldots q^{i_N}\right] &= \int \mathrm{d}^D\vec{x}\int \mathrm{d}^D\vec{y}\,\delta^{(D)}\left[\vec{y}-\vec{x}\right]\vec{x}^{i_1}\ldots\vec{x}^{i_N}K_{\text{in-in}}[\vec{y},t;\vec{x},t'] \\
&= \int \mathrm{d}^D\vec{x}\vec{x}^{i_1}\ldots\vec{x}^{i_N}K_{\text{in-in}}[\vec{x},t;\vec{x},t'];
\end{aligned}$$

where

$$\begin{aligned}
K_{\text{in-in}}[\vec{x},t;\vec{x},t'] &\equiv \frac{1}{i^N}\frac{\delta^N}{\delta J^+_{i_1}[t]\ldots\delta J^+_{i_N}[t]}\bigg|_{\vec{J}^+=\vec{J}^-=0}\int \mathrm{d}^D\vec{x}'\int \mathrm{d}^D\vec{y}'\int_{\vec{x}'}^{\vec{x}}\mathcal{D}\vec{q}_+\int_{\vec{y}'}^{\vec{x}}\mathcal{D}\vec{q}_-\widehat{\rho}[\vec{x}',\vec{y}'] \\
&\qquad\times\exp\left[i\int_{t'}^{t}\left(L[\vec{q}_+,\dot{\vec{q}}_+]-L[\vec{q}_-,\dot{\vec{q}}_-]+\vec{J}^+\cdot\vec{q}_+-\vec{J}^-\cdot\vec{q}_-\right)\mathrm{d}\tau\right] \\
&\equiv \frac{1}{(-i)^N}\,\frac{\delta^N}{\delta J^-_{i_1}[t]\ldots\delta J^-_{i_N}[t]}\bigg|_{\vec{J}^+=\vec{J}^-=0}\int \mathrm{d}^D\vec{x}'\int \mathrm{d}^D\vec{y}'\int_{\vec{x}'}^{\vec{x}}\mathcal{D}\vec{q}_+\int_{\vec{y}'}^{\vec{x}}\mathcal{D}\vec{q}_-\widehat{\rho}[\vec{x}',\vec{y}'] \\
&\qquad\times\exp\left[i\int_{t'}^{t}\left(L[\vec{q}_+,\dot{\vec{q}}_+]-L[\vec{q}_-,\dot{\vec{q}}_-]+\vec{J}^+\cdot\vec{q}_+-\vec{J}^-\cdot\vec{q}_-\right)\mathrm{d}\tau\right].
\end{aligned}$$

At this point, we may perform a change of variables,

$$\vec{q}^{\pm}\to\vec{q}^{\pm}_{\text{cl}}+\vec{\xi}^{\pm};$$

where the "classical" portion $\vec{q}_{\rm cl}^{\pm}$ obeys the boundary conditions

$$\begin{aligned} \vec{q}_{\rm cl}^{+}[t'] &= \vec{x}', & \vec{q}_{\rm cl}^{+}[t] &= \vec{x} \\ \vec{q}_{\rm cl}^{-}[t'] &= \vec{y}', & \vec{q}_{\rm cl}^{-}[t] &= \vec{x} \end{aligned}$$

and the quantum fluctuations $\vec{\xi}$ obey

$$\vec{\xi}^{\pm}[t] = \vec{\xi}^{\pm}[t'] = \vec{0}.$$

Heisenberg Picture Expressed in terms of the initial density operator

$$\widehat{\rho}_0 \equiv \sum_{\psi} p_\psi \left|\psi[t']\right\rangle \left\langle\psi[t']\right|, \tag{20.0.2}$$

we have

$$\begin{aligned} \langle\langle O \rangle\rangle = \mathrm{Tr}\left[O_s \widehat{\rho}[t]\right] &= \mathrm{Tr}\left[O_s U[t,t'] \widehat{\rho}_0 U^\dagger[t,t']\right] & (20.0.3) \\ &= \mathrm{Tr}\left[U^\dagger[t,t'] O_s U[t,t'] \widehat{\rho}_0\right] \equiv \mathrm{Tr}\left[O_H[t] \widehat{\rho}_0\right]; & (20.0.4) \end{aligned}$$

where we have identified the relationship between Heisenberg picture operator and its Schrödinger counterpart as

$$O_H[t] \equiv U^\dagger[t,t'] O_s U[t,t']. \tag{20.0.5}$$

Example: SHO

20.1 Open Systems

Motivation If the Schrödinger equation is obeyed, as we have seen

$$\rho(t) = U(t,t')\rho(t')U(t,t')^\dagger. \tag{20.1.1}$$

If the time evolution operator U is governed by a time dependent Hamiltonian that fluctuates in time much more quickly than the density operator itself, we may obtain a time averaged version of the above equation:

$$\begin{aligned} \left\langle i\left|\rho(t)\right|j\right\rangle &= \overline{\left\langle i\left|U(t,t')\right|a\right\rangle \left\langle b\left|U(t,t')^\dagger\right|j\right\rangle} \left\langle a\left|\rho(t')\right|b\right\rangle & (20.1.2) \\ &\equiv K_{ij}{}^{a'b'}(t,t') \left\langle a\left|\rho(t')\right|b\right\rangle. & (20.1.3) \end{aligned}$$

Open Quantum Systems More generally, open quantum systems have density matrices obeying the same sort of equation. For simplicity we shall assume the statistical properties of K are time independent, so that $K = K(t-t')$.

$$\left\langle i\left|\rho(t)\right|j\right\rangle = K_{ij}{}^{a'b'}(t-t') \left\langle a\left|\rho(t')\right|b\right\rangle. \tag{20.1.4}$$

If ρ is to be Hermitian,

$$\begin{aligned} \left\langle j\left|\rho(t)\right|i\right\rangle &= K^*{}_{ij}{}^{a'b'}(t-t') \left\langle b\left|\rho(t')\right|a\right\rangle & (20.1.5) \\ &= K_{ji}{}^{ba}(t-t') \left\langle b\left|\rho(t')\right|a\right\rangle. & (20.1.6) \end{aligned}$$

In other words,

$$K^*{}_{ij}^{\ a'b'}(t-t') = K_{ji}^{\ \ ba}(t-t'). \tag{20.1.7}$$

If we demand $\mathrm{Tr}\,[\rho] = 1$ for all times,

$$1 = \sum_i K_{ii}^{\ \ a'b'}(t-t')\,\langle a\,|\rho(t')|\,b\rangle\,. \tag{20.1.8}$$

Since $\delta^{ab}\,\langle a\,|\rho(t')|\,b\rangle = 1$ and ρ is otherwise arbitrary,

$$\sum_i K_{ii}^{\ \ a'b'}(t-t') = \delta^{ab}. \tag{20.1.9}$$

If we view ia and jb as a pair of collective indices, eq. (20.1.7) may be viewed as the statement that K is Hermitian. That in turn implies, K itself must go as $K \sim \sum \lambda\,|\lambda\rangle\,\langle\lambda|$, where the eigenvalues $\{\lambda\}$ are real.

$$K_{ij}^{\ \ a'b'}(t-t') = \sum_{\mathrm{I}} \lambda_{\mathrm{I}} M[\mathrm{I}]_i^{\ a} M[\mathrm{I}]^\dagger{}_j^{\ b} \tag{20.1.10}$$

The eigenvalues $\{\lambda_{\mathrm{I}}\}$ and eigen-matrices $M[\mathrm{I}]$ both depend on time through the difference $t-t'$. Furthermore, these matrices must be orthonormal

$$\mathrm{Tr}\left[M[\mathrm{I}]M[\mathrm{J}]^\dagger\right] = \delta_{\mathrm{IJ}}. \tag{20.1.11}$$

and in terms of them eq. (20.1.9) reads

$$\sum_i K_{ii}^{\ \ a'b'}(t-t') = \sum_{\mathrm{I}} \lambda_{\mathrm{I}} \delta^i_j \overline{M[\mathrm{I}]_b^{\ j}} M[\mathrm{I}]_i^{\ a} \tag{20.1.12}$$

$$= \tag{20.1.13}$$

When $t = t'$, we need to recover $\rho(t) = \rho(t')$. This in turn implies

$$K_{ij}^{\ \ a'b'}(0) = \delta_i^{\ a}\delta_j^{\ b}. \tag{20.1.14}$$

This implies we may choose the first eigen-system at $t = t'$ to be

$$M[1]_i^{\ a} = \frac{\delta_i^{\ a}}{\sqrt{D}}, \qquad\qquad \lambda_1 = D; \tag{20.1.15}$$

where D is the dimension of the space of matrices $\{M[\mathrm{I}]_i^{\ a}\}$.

20.2 Properties of Initial Density Operator

In this section, we wish to study the properties of the initial density operator

$$\rho[t'] \equiv \sum_i p_i\,|\alpha_i\rangle\,\langle\alpha_i|\,. \tag{20.2.1}$$

Firstly, since p_i refers to the statistical probability, they must lie between 0 and 1. Therefore $\rho[t']$ must be Hermitian; and as we shall soon see, its eigenvalues must also lie between 0 and 1.

Next, while $\{|\alpha_i\rangle\}$ can be assumed to be unit norm, they are not necessarily orthogonal since they are distinct but otherwise arbitrary. We first recognize that $\mathrm{Tr}\,[\rho]$ is total probability, and since total probability must be unity,

$$\mathrm{Tr}\,[\rho[t']] = 1. \tag{20.2.2}$$

Choose an orthonormal basis $\{|i\rangle\}$ and perform the trace:

$$\mathrm{Tr}\,[\rho[t']] = \sum_{j=1}^{D_V} \sum_i p_i \,\langle j|\,\alpha_i\rangle\,\langle\alpha_i|\,j\rangle \tag{20.2.3}$$

$$= \sum_{j=1}^{D_V} \sum_i p_i \,\langle\alpha_i|\,j\rangle\,\langle j|\,\alpha_i\rangle = \sum_i p_i \,\langle\alpha_i|\,\alpha_i\rangle \tag{20.2.4}$$

$$= \sum_i p_i = 1. \tag{20.2.5}$$

Because $\{|\alpha_i\rangle\}$ are not necessarily orthogonal, they are not necessarily eigenvectors of ρ. However, the eigenvalues of $\rho[t']$ must necessarily be positive. Since $\rho[t']$ is Hermitian, it must be diagonalizable. Let $\rho\,|\lambda\rangle = \lambda\,|\lambda\rangle$ and assume $\{|\lambda\rangle\}$ are unit norm. Then,

$$\lambda = \langle\lambda\,|\rho[t']|\,\lambda\rangle \tag{20.2.6}$$

$$= \sum_i p_i \,\langle\lambda|\,\alpha_i\rangle\,\langle\alpha_i|\,\lambda\rangle = \sum_i p_i |\,\langle\lambda|\,\alpha_i\rangle\,|^2 \tag{20.2.7}$$

$$\leq \sum_i p_i \,\langle\lambda|\,\lambda\rangle\,\langle\alpha_i|\,\alpha_i\rangle = \sum_i p_i = 1. \tag{20.2.8}$$

Since $\lambda = \sum_i p_i |\,\langle\lambda|\,\alpha_i\rangle\,|^2$ and since probabilities must be non-negative, we must therefore conclude: the eigenvalues of $\rho[t']$ must lie between 0 and 1.

$$0 \leq \lambda \leq 1 \tag{20.2.9}$$

This also implies

$$0 \leq \ldots \lambda^4 \leq \lambda^3 \leq \lambda^2 \leq \lambda \leq 1. \tag{20.2.10}$$

Equality is achieved iff $\lambda = 0$ or 1. That is, if n and m are a pair of distinct positive integers, with $n < m$:

$$\lambda^n = \lambda^m \qquad \Leftrightarrow \qquad \lambda^n(1 - \lambda^{m-n}) = 0. \tag{20.2.11}$$

We may write the initial density operator through its spectral decomposition, where only the non-zero eigenvalues are involved:

$$\rho[t'] = \sum_{\lambda\neq 0} \lambda\,|\lambda\rangle\,\langle\lambda|\,. \tag{20.2.12}$$

The square of the initial density operator is

$$\rho[t']^2 = \sum_{\lambda \neq 0} \lambda^2 \left|\lambda\right\rangle \left\langle\lambda\right| . \tag{20.2.13}$$

The *purity* is defined as the trace of $\rho[t']^2$.

$$\mathrm{Tr}\left[\rho[t']^2\right] = \sum_{\lambda \neq 0} \lambda^2. \tag{20.2.14}$$

Suppose all the eigenvalues obey $\lambda^2 < \lambda$ then we must have – upon term-by-term comparison –

$$\mathrm{Tr}\left[\rho[t']^2\right] < \mathrm{Tr}\left[\rho[t']\right] = 1. \tag{20.2.15}$$

Suppose one eigenvalue λ' obeys $\lambda'^2 = \lambda' = 1$. Then since $\mathrm{Tr}\left[\rho[t']\right] = \sum_\lambda \lambda = 1 + \sum_{\lambda \neq \lambda'} \lambda = 1$, and since all the λ lie between 0 and 1, there must in fact be only λ' in the sum. Similar reasoning will tell us, it is not possible to have two or more λ' that obey $\lambda'^2 = \lambda' = 1$.

> Purity of the initial density operator, defined as $\mathrm{Tr}\left[\rho[t']^2\right]$, is unity iff $\rho[t'] = \left|\psi\right\rangle \left\langle\psi\right|$ describes to a pure state.

21 Scattering Theory

Microscopic (quantum) systems are usually studied by scattering experiments. For instance, Rutherford discovered the structure of (gold) atoms, that they have a heavy central nucleus, by scattering alpha particles off a gold foil. In this section we shall study scattering theory itself.

Setup We will assume that the object of study is the potential V generated by some isolated quantum system; for e.g., the electric potential generated by a nucleus. The Schrödinger equation for a particle scattering off such a potential is

$$\left(i\partial_t - \frac{\vec{P}^2}{2m}\right)|\psi\rangle = V(\vec{X})\,|\psi\rangle\,. \tag{21.0.1}$$

We will assume that $V(\vec{X})$ does not depend on time t and only on space $\vec{X}$, so we may focus only on positive energy stationary states – namely, replace

$$|\psi(t)\rangle \to e^{-iEt}\,|\psi\rangle\,, \qquad E>0; \tag{21.0.2}$$

and obtain

$$\left(2mE - \vec{P}^2\right)|\psi\rangle = 2mV(\vec{X})\,|\psi\rangle\,. \tag{21.0.3}$$

This allows the Schrödinger equation to be converted into an integral equation:

$$|\psi\rangle = |\psi_0\rangle + \left(2mE-\vec{P}^2\right)^{-1}(2mV(\vec{x})\psi(\vec{x}))\,; \tag{21.0.4}$$

where $|\psi_0\rangle$ is, for now, an arbitrary homogeneous solution to

$$\left(2mE - \vec{P}^2\right)|\psi_0\rangle = 0 \tag{21.0.5}$$

$$\left(2mE - \vec{P}^2\right)\int_{\mathbb{R}^3}\frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\left|\vec{k}\right\rangle\left\langle\vec{k}\right|\psi_0\Big\rangle = 0. \tag{21.0.6}$$

That tells us

$$\left\langle\vec{k}\right|\psi_0\Big\rangle = (2\pi)^3\delta^{(3)}(\vec{k}-\vec{q})\widetilde{\psi}_0(\vec{q})e^{i\vec{q}\cdot\vec{x}}, \qquad \vec{q}^2 = 2mE. \tag{21.0.7}$$

The inverse of the differential operator $q^2+\vec{\nabla}^2$ may be obtained via a Fourier transform:

$$\begin{aligned}\widetilde{G}(\vec{x}-\vec{x}';q^2) &\equiv \left\langle\vec{x}\left|\frac{1}{q^2+\vec{P}^2}\right|\vec{x}'\right\rangle \\ &= \int_{\mathbb{R}^3}\frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\int_{\mathbb{R}^3}\frac{\mathrm{d}^3\vec{k}'}{(2\pi)^3}\left\langle\vec{x}\right|\left.\vec{k}\right\rangle\left\langle\vec{k}\left|\frac{1}{q^2+\vec{P}^2}\right|\vec{k}'\right\rangle\left\langle\vec{k}'\right|\left.\vec{x}'\right\rangle \\ &= \int_{\mathbb{R}^3}\frac{\mathrm{d}^3\vec{k}}{(2\pi)^3}\frac{e^{i\vec{k}\cdot(\vec{x}-\vec{x}')}}{q^2-\vec{k}^2}, \qquad q\equiv\sqrt{2mE}=|\vec{q}|.\end{aligned} \tag{21.0.8}$$

Problem 21.1. Inverse Verify that eq. (21.0.8) is indeed the inverse of $(q^2+\vec{\nabla}^2)$; namely,

$$\left(q^2+\vec{\nabla}^2_{\vec{x}}\right)\widetilde{G}(\vec{x}-\vec{x}';q^2)=\left(q^2+\vec{\nabla}^2_{\vec{x}'}\right)\widetilde{G}(\vec{x}-\vec{x}';q^2)=\delta^{(3)}(\vec{x}-\vec{x}'). \tag{21.0.9}$$

This means we may write eq. (21.0.4) as

$$|\psi\rangle=|\psi_0\rangle+\frac{2m}{q^2+\vec{P}^2}\int \mathrm{d}^3\vec{x}'\,|\vec{x}'\rangle\left\langle\vec{x}'\left|V(\vec{X})\right|\psi\right\rangle \tag{21.0.10}$$

$$\psi(\vec{x})=\psi_0(\vec{x})+2m\int_{\mathbb{R}^3}\mathrm{d}^3\vec{x}'\widetilde{G}(\vec{x}-\vec{x}';q^2=2mE)V(\vec{x}')\psi(\vec{x}'), \tag{21.0.11}$$

because, if we apply $2mE+\vec{\nabla}^2$ on both sides, we recover the Schrödinger equation (21.0.3). Notice this is very much like solving an inhomogeneous ODE; the general solution consists of the homogeneous plus the particular solution.

The primary remaining issue is to compute $\widetilde{G}$ itself. First show that the 3D integral in eq. (21.0.8) can be reduced to a 1D one:

$$\widetilde{G}(\vec{x}-\vec{x}';q^2)=\frac{1}{R}\int_{-\infty}^{\infty}\frac{\mathrm{d}k\cdot k}{(2\pi)^2}\frac{\sin(kR)}{q^2-k^2},\qquad R\equiv|\vec{x}-\vec{x}'|. \tag{21.0.12}$$

We shall see that there are (at least) two possible solutions:

$$\widetilde{G}^{\pm}(qR)=-\frac{e^{\pm iqR}}{4\pi R}. \tag{21.0.13}$$

There is an ambiguity here. When integrating over k, there are two singularities at $k=\pm q$. This means we really need to choose a contour on the complex k plane to skirt them. □

Let us choose to skirt the pole at $k=-q$ by going 'under' it; and the $k=+q$ by going above it. Keeping in mind $R>0$,

$$\widetilde{G}(\vec{x}-\vec{x}';q^2)=\frac{1}{2iR}\int_{-\infty}^{\infty}\frac{\mathrm{d}k\cdot k}{(2\pi)^2}\frac{e^{ikR}-e^{-ikR}}{(q+k)(q-k)} \tag{21.0.14}$$

$$=\frac{2\pi i}{2iR(2\pi)^2}\left((+)(-q)\frac{e^{-iqR}}{2q}-(-)(+q)\frac{e^{-iqR}}{2q}\right) \tag{21.0.15}$$

$$=-\frac{e^{-iqR}}{4\pi R}. \tag{21.0.16}$$

We may check this result by noticing that, if we set $q=0$, $\widetilde{G}=-(4\pi R)^{-1}$. From the integral representation,

$$\widetilde{G}(\vec{x}-\vec{x}';q^2=0)=-\frac{1}{R}\int_{-\infty}^{\infty}\frac{\mathrm{d}k}{(2\pi)^2}\frac{\sin(kR)}{k} \tag{21.0.17}$$

$$=-\frac{1}{2\pi R}\int_{-\infty}^{\infty}\frac{\mathrm{d}k}{2\pi i}\frac{e^{ik}-e^{-ik}}{2k} \tag{21.0.18}$$

$$=-\frac{1}{4\pi R}. \tag{21.0.19}$$

Note that, if $\widetilde{G}$ is a solution to $(q^2+\vec{\nabla}^2)\widetilde{G}=\delta^{(3)}$, then for q^2 real, so is $\widetilde{G}^*$; that means we have shown that both expressions in eq. (21.0.13) are indeed solutions.

At this point, we may gather from eq. (21.0.11),

$$\psi(\vec{x})=e^{i\vec{q}\cdot\vec{x}}-2m\int_{\mathbb{R}^3}\mathrm{d}^3\vec{x}'\frac{e^{\pm iq|\vec{x}-\vec{x}'|}}{4\pi|\vec{x}-\vec{x}'|}V(\vec{x}')\psi(\vec{x}'). \tag{21.0.20}$$

If we put back the e^{-iEt} and assume the V is localized enough that we may take the far zone limit, namely when

$$r\equiv|\vec{x}|\gg|\vec{x}'|\equiv r' \qquad \text{and} \qquad qr\gg 1. \tag{21.0.21}$$

From the Taylor expansion

$$\begin{aligned}|\vec{x}-\vec{x}'|&\approx|\vec{x}|-\vec{x}'\cdot\widehat{r}+\ldots\\&\approx r\left(1-\frac{\vec{x}'\cdot\widehat{r}}{r}+\mathcal{O}\left((r'/r)^2\right)\right)\end{aligned} \tag{21.0.22}$$

we have

$$\frac{e^{\pm iq|\vec{x}-\vec{x}'|}}{4\pi|\vec{x}-\vec{x}'|}\approx\frac{e^{\pm iq(r-\vec{x}'\cdot\widehat{r}+\ldots)}}{4\pi r}\left(1+\mathcal{O}\left(\frac{r'}{r}\right)\right). \tag{21.0.23}$$

Therefore, in the far zone,

$$e^{-iEt}\psi(\vec{x})\to e^{i(\vec{q}\cdot\vec{x}-Et)}+\frac{e^{\pm iq(r\mp(E/q)t)}}{r}f \tag{21.0.24}$$

$$f(q\widehat{r})\equiv-\frac{2m}{4\pi}\int_{\mathbb{R}^3}\mathrm{d}^3\vec{x}'e^{-iq\widehat{r}\cdot\vec{x}'}V(\vec{x}')\psi(\vec{x}') \tag{21.0.25}$$

This far zone expression in eq. (21.0.24) allows the following interpretation. The first term on the RHS corresponds to a plane wave. Next, by choosing $\widetilde{G}=e^{+iqR}/(4\pi R)$, we obtain for the second term on the RHS an outgoing spherical wave propagating to infinity. Whereas, by choosing $\widetilde{G}=e^{-iqR}/(4\pi R)$, we obtain for the second term on the RHS an ingoing spherical wave. For scattering theory, we shall therefore choose $\widetilde{G}=e^{+iqR}/(4\pi R)$, so that we may assert, the homogeneous solution (1st term on RHS) is the 'incoming' plane wave, which then scatters off the central potential V, then proceeds to propagate outwards to infinity (as described by the 2nd term on the RHS).

$$\psi(\vec{x})=e^{i\vec{q}\cdot\vec{x}}-2m\int_{\mathbb{R}^3}\mathrm{d}^3\vec{x}'\frac{e^{iq|\vec{x}-\vec{x}'|}}{4\pi|\vec{x}-\vec{x}'|}V(\vec{x}')\psi(\vec{x}'). \tag{21.0.26}$$

Before moving on, let us provide a more involved but more systematic derivation of eq. (21.0.24). Firstly,

$$\frac{e^{\pm iq|\vec{x}-\vec{x}'|}}{4\pi|\vec{x}-\vec{x}'|}=\pm\sum_{\ell'=0}^{\infty}iqj_{\ell'}(qr_<)h_{\ell'}^{\left(\frac{1}{2}\right)}(qr_>)\sum_{m'=-\ell'}^{\ell'}Y_{\ell'}^{m'}(\widehat{x})\overline{Y_{\ell'}^{m'}(\widehat{x}')} \tag{21.0.27}$$

$$h_\ell^{(1)}(x \gg 1) \to (-i)^{\ell+1}\frac{e^{ix}}{x}\left(1+\mathcal{O}(x^{-1})\right) \tag{21.0.28}$$

Moreover,

$$e^{\pm i\vec{k}\cdot\vec{x}} = 4\pi\sum_{\ell'=0}^{\infty}(\pm i)^{\ell'}j_{\ell'}(kr)\sum_{m'=-\ell'}^{\ell'}Y_{\ell'}^{m'}(\widehat{x})\overline{Y_{\ell'}^{m'}(\widehat{k})}. \tag{21.0.29}$$

That means in the far zone, i.e., keeping only $1/r$,

$$\frac{e^{iq|\vec{x}-\vec{x}'|}}{4\pi|\vec{x}-\vec{x}'|} \to \sum_{\ell'=0}^{\infty} iqj_{\ell'}(qr')(-i)^{\ell'+1}\frac{e^{iqr}}{qr}\sum_{m'=-\ell'}^{\ell'}Y_{\ell'}^{m'}(\widehat{x})\overline{Y_{\ell'}^{m'}(\widehat{x}')} \tag{21.0.30}$$

$$= \frac{e^{iqr}}{4\pi r}\sum_{\ell'=0}^{\infty}4\pi(-i)^{\ell'}j_{\ell'}(qr')\sum_{m'=-\ell'}^{\ell'}Y_{\ell'}^{m'}(\widehat{x})\overline{Y_{\ell'}^{m'}(\widehat{x}')} \tag{21.0.31}$$

$$= \frac{e^{iq(r-\widehat{x}\cdot\vec{x}')}}{4\pi r} \tag{21.0.32}$$

Cross Sections & Probability Current One of the key observables in scattering experiments is the differential cross section.

Consider a parallel beam of particles zipping down an accelerator tunnel. If L denotes flux of particles (number of particles per unit time per unit area) across some infinitesimal cross sectional area $\mathrm{d}\sigma$, so that the number of particles per unit time crossing it is $\mathrm{d}N = L\mathrm{d}\sigma$, then the differential cross section is defined by the number of particles scattered into a given infinitesimal solid angle $\mathrm{d}\Omega$ divided by the luminosity L:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \equiv \frac{\text{Number of outgoing particles per solid angle}}{\text{Number of incident particles per unit time per unit area}} \tag{21.0.33}$$

$$= \frac{1}{L}\frac{\mathrm{d}N}{\mathrm{d}\Omega}. \tag{21.0.34}$$

This definition is consistent with how cross section is actually measured: L is set by the parameters of the accelerator setup, whereas $\mathrm{d}N/\mathrm{d}\Omega$ involves counting particles. Moreover, in our quantum mechanical context, the flux of particles can be computed through the probability current $\vec{J}$, defined as

$$\vec{J}(t,\vec{x}) \equiv \frac{i}{2m}\left(\psi\vec{\nabla}\psi^* - \psi^*\vec{\nabla}\psi\right). \tag{21.0.35}$$

Problem 21.2. Probability Conservation Law To check that $\vec{J}$ is indeed a probability current, verify using the Schrödinger equation its conservation law:

$$\partial_t|\psi|^2 = -\vec{\nabla}\cdot\vec{J}, \tag{21.0.36}$$

which states that the rate of change of probability $|\psi|^2$ within an infinitesimal volume must be equal to the negative rate of flow out the said volume. That is, if there is a net flow *out* of the volume, there must be a decrease in $|\psi|^2$; whereas if there is a note flow *into* the volume, there must be an increase. □

We may interpret $\vec{J}\cdot\widehat{n}$ as the number of particles following through the surface normal to the unit vector $\widehat{n}$ per unit time per unit area; moreover, recall that $r^2\mathrm{d}\Omega$ is the area element of a sphere of radius r. Therefore, in the far zone $qr \gg 1$,

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \equiv \frac{\text{Number of outgoing particles per solid angle}}{\text{Number of incident particles per unit time per unit area}} \tag{21.0.37}$$

$$= \frac{\lim_{r\to\infty} r^2(\vec{J}_{\text{outgoing}}\cdot\widehat{r})}{\vec{J}_{\text{incident}}\cdot\widehat{q}} \tag{21.0.38}$$

We can compute the numerator and denominator as follows

$$\lim_{r\to\infty} r^2\widehat{r}\cdot\vec{J}_{\text{outgoing}} = \lim_{r\to\infty}\frac{r^2}{2m}\lim_{r\to\infty}\widehat{r}\cdot\left(i\frac{e^{iqr}}{r}f\vec{\nabla}\left(\frac{e^{-iqr}}{r}f^*\right)+\text{c.c.}\right) \tag{21.0.39}$$

$$\widehat{q}\cdot\vec{J}_{\text{incoming}} = \frac{\widehat{q}}{2m}\cdot\left(ie^{i\vec{q}\cdot\vec{x}}\vec{\nabla}e^{-i\vec{q}\cdot\vec{x}}+\text{c.c.}\right). \tag{21.0.40}$$

Problem 21.3. Show that eq. (21.0.38) yields

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f|^2. \tag{21.0.41}$$

Note that f depends on $\widehat{r}$; recall eq. (21.0.24). The $r\to\infty$ limit is important here. □

Born Approximation Apart from allowing us to choose the outgoing boundary conditions readily, converting the Schrödinger PDE into an integral equation allows us to find approximate solutions via repeated iteration. That is, we suppose the 2nd term on the RHS is 'small'. Then, we may iterate the RHS into itself:

$$\psi(\vec{x}) = e^{i\vec{q}\cdot\vec{x}} - 2m\int_{\mathbb{R}^3}\mathrm{d}^3\vec{x}'\frac{e^{iq|\vec{x}-\vec{x}'|}}{4\pi|\vec{x}-\vec{x}'|}V(\vec{x}')e^{i\vec{q}\cdot\vec{x}'} + \mathcal{O}(V^2). \tag{21.0.42}$$

We have suppressed the $\mathcal{O}(V^2)$ term that contains $\psi(\vec{x})$. If that term is small relative to the $\mathcal{O}(V^1)$ term, however, we may discard the former and obtain the first Born approximation solution to ψ.

$$\psi(\vec{x}) \approx e^{i\vec{q}\cdot\vec{x}} - 2m\int_{\mathbb{R}^3}\mathrm{d}^3\vec{x}'\frac{e^{iq|\vec{x}-\vec{x}'|}}{4\pi|\vec{x}-\vec{x}'|}V(\vec{x}')e^{i\vec{q}\cdot\vec{x}'} \tag{21.0.43}$$

$$|\vec{q}| = \sqrt{2mE} = q. \tag{21.0.44}$$

At this point, upon taking the far zone limit,

$$\psi(qr\gg 1,\widehat{x}) \to e^{i\vec{q}\cdot\vec{x}} + \frac{e^{iqr}}{r}f(\widehat{x}) \tag{21.0.45}$$

$$f(\vec{q},q\widehat{x}) = -\frac{2m}{4\pi}\int_{\mathbb{R}^3}\mathrm{d}^3\vec{x}'V(\vec{x}')e^{iq(\widehat{q}-\widehat{x})\cdot\vec{x}'} \tag{21.0.46}$$

$$= -2m\int_{\mathbb{R}^3}\mathrm{d}^3\vec{x}'\sum_{\ell=0}^{\infty}V_\ell^m(r')Y_\ell^m(\widehat{x}') \tag{21.0.47}$$

$$\times \sum_{\ell'=0}^{\infty} (-i)^{\ell'} j_{\ell'}(qr') \sum_{m'=-\ell'}^{\ell'} Y_{\ell'}^{m'}(\widehat{x}) \overline{Y_{\ell'}^{m'}(\widehat{x}')} \tag{21.0.48}$$

$$\times \sum_{\ell''=0}^{\infty} i^{\ell''} j_{\ell''}(qr') \sum_{m''=-\ell''}^{\ell''} Y_{\ell''}^{m''}(\widehat{x}') \overline{Y_{\ell''}^{m''}(\widehat{q})} \tag{21.0.49}$$

$$V(\vec{x}') \equiv \sum_{\ell=0}^{\infty} V_\ell^m(r') Y_\ell^m(\widehat{x}'). \tag{21.0.50}$$

Spherically Symmetric V For a spherically symmetric central potential, namely $V(\vec{x}) = V(r)$,

$$f(\vec{q}, q\widehat{x}) = -\frac{2m}{4\pi} \int_{\mathbb{R}^3} \mathrm{d}^3\vec{x}' e^{i(\vec{q}-q\widehat{r})\cdot\vec{x}'} V(r') \tag{21.0.51}$$

$$= -2m \int_0^\infty \mathrm{d}r' r'^2 V(r') \sum_{\ell'=0}^{\infty} j_{\ell'}(qr')^2 \sum_{m'=-\ell'}^{\ell'} Y_{\ell'}^{m'}(\widehat{x}') \overline{Y_{\ell'}^{m'}(\widehat{q})}. \tag{21.0.52}$$

We can also do the first integral directly, by reducing it to a 1D one.

$$f(\vec{q}, q\widehat{x}) = -m \int_0^\infty \mathrm{d}r' r'^2 \int_{-1}^{+1} e^{i|\vec{q}-q\widehat{r}|r'c} V(r') \tag{21.0.53}$$

$$= -m \int_0^\infty \mathrm{d}r' r'^2 V(r') \frac{e^{i|\vec{q}-q\widehat{r}|r'} - e^{-i|\vec{q}-q\widehat{r}|r'}}{i|\vec{q}-q\widehat{r}|r'} \tag{21.0.54}$$

$$= -2m \int_0^\infty \mathrm{d}r' r' V(r') \frac{\sin\left(\sqrt{2}qr'\sqrt{1-\widehat{q}\cdot\widehat{x}}\right)}{\sqrt{2}q\sqrt{1-\widehat{q}\cdot\widehat{x}}} \tag{21.0.55}$$

Note that, if we define $\cos\theta \equiv \widehat{q}\cdot\widehat{x}$,

$$\sqrt{2}\sqrt{1-\widehat{q}\cdot\widehat{x}} = \sqrt{4\sin^2(\theta/2)} = 2\sin(\theta/2). \tag{21.0.56}$$

Consider, as Sakurai does, the Yukawa potential

$$V = U_0 \frac{e^{-\mu r}}{r}. \tag{21.0.57}$$

Within the first Born approximation,

$$f(\vec{q}, q\widehat{x}) = -2mU_0 \mathrm{Im} \int_0^\infty \mathrm{d}r' r' \frac{e^{-\mu r'}}{r'} \frac{e^{i2qr'\sin(\theta/2)}}{2q\sin(\theta/2)} \tag{21.0.58}$$

$$= -\frac{mU_0}{q\sin(\theta/2)} \mathrm{Im} \int_0^\infty \mathrm{d}r' e^{-\mu r' + i2qr'\sin(\theta/2)} \tag{21.0.59}$$

$$= -\frac{mU_0}{q\sin(\theta/2)} \frac{2q\sin\left(\frac{\theta}{2}\right)}{\mu^2 - 2q^2\cos(\theta) + 2q^2} = -\frac{2mU_0}{\mu^2 - 2q^2\cos(\theta) + 2q^2} \tag{21.0.60}$$

The scattering cross section for scattering off a Coulomb potential can be gotten by setting $\mu \to 0$.

$$\frac{\mathrm{d}\sigma[\text{Coulomb}]}{\mathrm{d}\Omega} = \frac{(2mU_0)^2}{16q^4 \sin^4(\theta/2)} \tag{21.0.61}$$

This is what Rutherford found.

Problem 21.4. Dipole-Yukawa Potential Consider the scattering off the following potential

$$V = U_0 \frac{e^{-\mu r}}{r^2} Y_1^0(\theta, \phi). \tag{21.0.62}$$

Find the differential cross section within the first Born approximation in terms of spherical harmonics:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \sum_{\ell_1, m_1} \sum_{\ell_2, m_2} g_{\ell_1, m_1}^{\ell_2, m_2} \cdot Y_{\ell_1}^{m_1}(\widehat{r}) Y_{\ell_2}^{m_2}(\widehat{q}). \tag{21.0.63}$$

Can you take the $\mu \to 0$ limit?

Hint: This problem involves the addition of angular momentum. Try to push the analysis as far as you can. □

22 Acknowledgments

A Classical Mechanics of a Point Particle: Review

In this section, I shall provide a review of the classical mechanics of point particles.

Lagrangian Mechanics Let us start by assuming the variational principle, which is encapsulated within the Lagrangian L. We shall suppose L only depends on the trajectory $\vec{q}(t)$ and its velocity $\dot{\vec{q}}(t)$, but not on its higher time derivatives.

The extremum of the action leads to the Euler-Lagrange equations

$$\frac{\partial L}{\partial q^i} = \frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial L}{\partial \dot{q}^i}. \tag{A.0.1}$$

Hamiltonian Dynamics The momentum conjugate to $\vec{q}$ is defined as

$$p_i \equiv \frac{\partial L(\vec{q}, \dot{\vec{q}})}{\partial \dot{q}^i}. \tag{A.0.2}$$

This eq. (A.0.2) will usually allow us to solve $\dot{\vec{q}}$ in terms of $\vec{q}$ and $\vec{p}$. In turn, the Hamiltonian is defined as

$$H(\vec{q}, \vec{p}) = p_i \dot{q}^i(\vec{q}, \vec{p}) - L\left(\vec{q}, \vec{p}\right). \tag{A.0.3}$$

Note that, since we have switched variables from $(\vec{q}, \dot{\vec{q}})$ to $(\vec{q}, \vec{p})$, we need to understand how the partial derivatives in eq. (A.0.1) are altered. Viewed as a function of $(\vec{q}, \dot{\vec{q}})$,

$$\begin{aligned}\delta H(\vec{q}, \dot{\vec{q}}) &= \delta p_i \dot{q}^i + p_i \delta \dot{q}^i - \left(\frac{\partial L(\vec{q}, \dot{\vec{q}})}{\partial q^i}\right)_{\dot{\vec{q}}} \delta q^i - \left(\frac{\partial L(\vec{q}, \dot{\vec{q}})}{\partial \dot{q}^i}\right)_{\vec{q}} \delta \dot{q}^i \\ &= \delta p_i \dot{q}^i + p_i \delta \dot{q}^i - \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L(\vec{q}, \dot{\vec{q}})}{\partial \dot{q}^i}\right)_{\dot{\vec{q}}} \delta q^i - p_i \delta \dot{q}^i \\ &= \delta p_i \dot{q}^i - \dot{p}_i \delta q^i \end{aligned} \tag{A.0.4}$$

Whereas, when viewed as a function of $(\vec{q}, \vec{p})$,

$$\delta H(\vec{q}, \vec{p}) = \left(\frac{\partial H}{\partial q^i}\right)_{\vec{p}} \delta q^i + \left(\frac{\partial H}{\partial p^i}\right)_{\vec{q}} \delta p^i. \tag{A.0.5}$$

Comparing the two expressions then hands us Hamilton's equations:

$$\dot{q}^i = \frac{\partial H(\vec{q}, \vec{p})}{\partial p^i}, \tag{A.0.6}$$

$$\dot{p}_i = -\frac{\partial H(\vec{q}, \vec{p})}{\partial q^i}. \tag{A.0.7}$$

Poisson brackets & Hamiltonian flow The Poisson bracket between two functions (f, g) of $(\vec{q}, \vec{p})$ is defined as

$$\{f, g\}_{\mathrm{PB}} \equiv \frac{\partial f(\vec{q}, \vec{p})}{\partial q^i}\frac{\partial g(\vec{q}, \vec{p})}{\partial p_i} - \frac{\partial f(\vec{q}, \vec{p})}{\partial p_i}\frac{\partial g(\vec{q}, \vec{p})}{\partial q^i}. \tag{A.0.8}$$

We now see that, using these Poisson brackets, that the Hamilton 'generates' time evolution:

$$\begin{aligned}\{f, H\}_{\mathrm{PB}} &= \frac{\partial f}{\partial q^i}\frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p^i}\frac{\partial H}{\partial q_i} \\ &= \frac{\partial f}{\partial q^i}\dot{q}^i + \frac{\partial f}{\partial p^i}\dot{p}_i = \frac{\mathrm{d} f\left(\vec{q}(t), \vec{p}(t)\right)}{\mathrm{d}t}. \end{aligned} \tag{A.0.9}$$

Spatial translations & Momentum flow Using the Poisson brackets, we may also show that momentum generates spatial displacements in that

$$\begin{aligned}\{f, p_\ell\}_{\mathrm{PB}} &= \frac{\partial f}{\partial q^i}\frac{\partial p_\ell}{\partial p_i} - \frac{\partial f}{\partial p^i}\frac{\partial p_\ell}{\partial q_i} \\ &= \frac{\partial f}{\partial q^\ell}. \end{aligned} \tag{A.0.10}$$

Electromagnetism of Point Particles In Minkowski spacetime, the relativistic action for a point electric charge e is given by

$$S = \int \mathrm{d}t \left(-m\sqrt{1 - \vec{v}^2} + e\vec{A} \cdot \vec{v} - e\phi\right). \tag{A.0.11}$$

Here, m is its mass; $\vec{v} \equiv \mathrm{d}\vec{q}/\mathrm{d}t$ its spatial velocity; $\vec{A}$ is the vector potential; and $\phi \equiv A_0$ is the electric potential (and also the zeroth component of the vector potential). In the non-relativistic limit, we have

$$S = \int \mathrm{d}t \left(-m + L_{\mathrm{EM}} + \mathcal{O}(v^4)\right), \tag{A.0.12}$$

where the Lagrangian is

$$L_{\mathrm{EM}} \equiv \frac{m}{2}\vec{v}^2 + e\vec{A}\cdot\vec{v} - e\phi. \tag{A.0.13}$$

Problem A.1. Electromagnetic Hamiltonian Using the definition in eq. (A.0.2), namely

$$\vec{p} \equiv \frac{\partial L_{\mathrm{EM}}}{\partial \vec{v}}, \tag{A.0.14}$$

show that

$$\vec{v} = \frac{1}{m}\left(\vec{p} - e\vec{A}\right). \tag{A.0.15}$$

From this result, show that the Hamiltonian H_{EM} associated with the electromagnetic Lagrangian in eq. (A.0.13) is

$$H_{\mathrm{EM}} = \frac{1}{2m}\left(\vec{p} - e\vec{A}\right)^2 + e\phi. \tag{A.0.16}$$

Eq. (A.0.16) is often the starting point of electromagnetism in the quantum mechanics. □

We may check the consistency of the classical Hamiltonian in eq. (A.0.16) by computing its Hamilton's equations. Applying eq. (A.0.6) recovers eq. (A.0.15); while employing eq. (A.0.7) yields

$$\dot{\vec{p}} = -\frac{\partial H_{\mathrm{EM}}}{\partial \vec{q}} = -\frac{1}{m}\left(p_i - eA_i\right)(-e)\vec{\nabla}_{\vec{q}}A_i - e\vec{\nabla}_{\vec{q}}\phi. \tag{A.0.17}$$

Utilizing eq. (A.0.15) once again,

$$\dot{\vec{p}} = ev_i\vec{\nabla}_{\vec{q}}A_i - e\vec{\nabla}_{\vec{q}}\phi \tag{A.0.18}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(m\vec{v} + e\vec{A}(t,\vec{q})\right) = ev^i\vec{\nabla}_{\vec{q}}A^i - e\vec{\nabla}_{\vec{q}}\phi. \tag{A.0.19}$$

Now, $\mathrm{d}\vec{A}/\mathrm{d}t = \partial_t\vec{A} + v^a\partial_a\vec{A}$. Hence, we arrive at

$$m\dot{v}^i = e\left(v^m\partial_i A^m - v^m\partial_m A^i - \partial_t A^i - \partial_i\phi\right). \tag{A.0.20}$$

If we remember the relationship between the electric and magnetic fields with that of the vector potential, namely

$$E^i = -\partial_i\phi - \partial_t A^i \qquad \text{and} \qquad B^i = \epsilon^{imn}\partial_m A^n, \tag{A.0.21}$$

we recover the familiar Lorentz force law:

$$m\dot{v}^i = e\left(E^i + (\vec{v}\times\vec{B})^i\right). \tag{A.0.22}$$

Problem A.2. Use the result

$$\epsilon^{ijk}\epsilon^{kmn} = \delta^i_{[m}\delta^j_{n]} \tag{A.0.23}$$

to demonstrate that

$$(\vec{v} \times \vec{B})^i = v^m \partial_i A^m - v^m \partial_m A^i. \tag{A.0.24}$$

This connects eq. (A.0.20) to eq. (A.0.22). □

B Some Identities

For linear operators A, B, and C,

$$[AB, C] = A[B, C] + [A, C]B \tag{B.0.1}$$

$$[A, B]^\dagger = -[A^\dagger, B^\dagger]. \tag{B.0.2}$$

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