Quantum Mechanics Notes

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1 Approximation methods

1(a) Time-independent perturbation theory

Time-independent perturbation theory lets us study Hamiltonians of the form $H = H_0 + \lambda H'$ where H_0 is a Hamiltonian that we can solve exactly and H' is some change (a "perturbation") that we're interested in. λ is a constant scalar; we will come up with an approximation that is good for small enough values of λ.

Our goal is to approximate the eigenstates $|\psi\rangle$ and eigenvalues E of the eigenvalue problem

$$H\,|\psi\rangle = E\,|\psi\rangle\,.$$

One could imagine that there might be some states $\left|\psi^{(m)}\right\rangle$ and values $E^{(m)}$ so that we can write

$$|\psi\rangle = \left|\psi^{(0)}\right\rangle + \lambda\left|\psi^{(1)}\right\rangle + \lambda^2\left|\psi^{(2)}\right\rangle + \cdots \tag{1}$$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots \tag{2}$$

for small enough λ. We will assume that some approximation of this type works and then try to determine what the $\left|\psi^{(m)}\right\rangle$ and $E^{(m)}$ must be.

Gap!!! There should be some justification of whether/why the series above converge and an explanation of the theory of asymptotic approximations that allows us to make these approximations even when the series diverge.

In our derivations, let us suppose that H_0 has eigenstates $|n\rangle$ and eigenvalues $E_n^{(0)}$ for $n = 1, 2, 3, \ldots$, that is,

$$H_0\,|n\rangle = E_n^{(0)}\,|n\rangle\,,\ n = 1, 2, 3, \ldots.$$

Perturbation theory also works for continuous spectra but it will keep our notation simpler to talk about the discrete case.

1(a).1 The zero-order energies

As $\lambda \to 0$, we should have $E \to E_n^{(0)}$ for some n. Looking at (2), we must have $\boxed{E^{(0)} = E_n^{(0)}.}$ This suggests that we give our state an index. From now on, let's write $|\psi_n\rangle$ instead of $|\psi\rangle$, E_n instead of E, $\left|\psi_n^{(m)}\right\rangle$ instead of $\left|\psi^{(m)}\right\rangle$, and $E_n^{(m)}$ instead of $E^{(m)}$. We have

$$|\psi_n\rangle = \left|\psi_n^{(0)}\right\rangle + \lambda\left|\psi_n^{(1)}\right\rangle + \lambda^2\left|\psi_n^{(2)}\right\rangle + \cdots \tag{3}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \tag{4}$$

(For a degenerate spectrum, there could be multiple possible n—just choose one. It turns out that we are able to make this one-to-one map between eigenstates of H_0 and eigenstates of H but there are multiple possible maps because we could choose any of the states with energy E_n.)

1(a).2 The zero-order states

Now, we have $H_0\,|\psi\rangle = E_n^{(0)}\,|\psi\rangle$, so $|\psi_n\rangle$ is an eigenstate of H_0 with eigenvalue $E_n^{(0)}$, so $|\psi_n\rangle$ is a superposition of the states that have energy $E_n^{(0)}$. Let D_n be the set of indices m such that $E_m^{(0)} = E_n^{(0)}$. Then we can write

$$|\psi_n\rangle = \sum_{m \in D_n} c_m\,|m\rangle$$

for some coefficients c_m. To find the c_m, we turn to the Schrödinger equation. We have

$$\begin{aligned}
\left(H_0+\lambda H'\right)|\psi_n\rangle &= E_n|\psi_n\rangle \\
\left(H_0+\lambda H'\right)\left[\left|\psi_n^{(0)}\right\rangle+\lambda\left|\psi_n^{(1)}\right\rangle+\mathcal{O}(\lambda^2)\right] &= \left(E_n^{(0)}+\lambda E_n^{(1)}+\mathcal{O}(\lambda^2)\right)\left[\left|\psi_n^{(0)}\right\rangle+\lambda\left|\psi_n^{(1)}\right\rangle+\mathcal{O}(\lambda^2)\right] \\
H_0\left|\psi_n^{(0)}\right\rangle+\lambda\left(H'\left|\psi_n^{(0)}\right\rangle+H_0\left|\psi_n^{(1)}\right\rangle\right)+\mathcal{O}(\lambda^2) &= E_n^{(0)}\left|\psi_n^{(0)}\right\rangle+\lambda\left(E_n^{(0)}\left|\psi_n^{(1)}\right\rangle+E_n^{(1)}\left|\psi_n^{(0)}\right\rangle\right)+\mathcal{O}(\lambda^2).
\end{aligned}$$

In the zeroth order of λ this gives $H_0\left|\psi_n^{(0)}\right\rangle = E_n^{(0)}\left|\psi_n^{(0)}\right\rangle$, confirming what we already know: $\left|\psi_n^{(0)}\right\rangle$ is an eigenstate of H_0 with eigenvalue $E_n^{(0)}$. In the first order of λ we get

$$H'\left|\psi_n^{(0)}\right\rangle+H_0\left|\psi_n^{(1)}\right\rangle = E_n^{(0)}\left|\psi_n^{(1)}\right\rangle+E_n^{(1)}\left|\psi_n^{(0)}\right\rangle.$$

Multiplying with $\langle m|$, where $m\in D_n$,

$$\begin{aligned}
\langle m|H'\left|\psi_n^{(0)}\right\rangle+\langle m|H_0\left|\psi_n^{(1)}\right\rangle &= E_n^{(0)}\left\langle m|\psi_n^{(1)}\right\rangle+E_n^{(1)}\left\langle m|\psi_n^{(0)}\right\rangle \\
\langle m|H'\left|\psi_n^{(0)}\right\rangle+\cancel{E_m^{(0)}\left\langle m|\psi_n^{(1)}\right\rangle} &= \cancel{E_n^{(0)}\left\langle m|\psi_n^{(1)}\right\rangle}+E_n^{(1)}\left\langle m|\psi_n^{(0)}\right\rangle \\
\left\langle m|\psi_n^{(0)}\right\rangle &= \frac{\langle m|H'\left|\psi_n^{(0)}\right\rangle}{E_n^{(1)}}.
\end{aligned}$$

Gap!!! This part needs to be added. It should include discussion of the orthonormality of the states.

1(a).3 Rearranging the Schrödinger equation

To get the first- and second-order corrections, we start by multiplying the Schrödinger equation by $\left\langle\psi_m^{(0)}\right|$. We get

$$\begin{aligned}
\left\langle\psi_m^{(0)}\right|\left(H_0+\lambda H'\right)|\psi_n\rangle &= E_n\left\langle\psi_m^{(0)}|\psi_n\right\rangle \\
E_m^{(0)}\left\langle\psi_m^{(0)}|\psi_n\right\rangle+\left\langle\psi_m^{(0)}\right|\lambda H'|\psi_n\rangle &= E_n\left\langle\psi_m^{(0)}|\psi_n\right\rangle \\
\left\langle\psi_m^{(0)}|\psi_n\right\rangle &= \frac{\left\langle\psi_m^{(0)}\right|\lambda H'|\psi_n\rangle}{E_n-E_m^{(0)}} \\
\left\langle\psi_m^{(0)}|\psi_n\right\rangle &= \frac{\lambda\left\langle\psi_m^{(0)}\right|H'\left(\left|\psi_n^{(0)}\right\rangle+\lambda\left|\psi_n^{(1)}\right\rangle+\mathcal{O}(\lambda^2)\right)}{E_n-E_m^{(0)}} \qquad (5)
\end{aligned}$$

Let's examine the denominator. We'll consider the two cases where n is/is not degenerate with m.

Let D_n be the set of indices m such that $E_m^{(0)}=E_n^{(0)}$. If $m\notin D_n$ then

$$\begin{aligned}
E_n-E_m^{(0)} &= \left(E_n^{(0)}-E_m^{(0)}\right)+\lambda E_n^{(1)}+\lambda^2E_n^{(1)}+\mathcal{O}(\lambda^3) \\
&= \left(E_n^{(0)}-E_m^{(0)}\right)\left[1+\mathcal{O}(\lambda)\right].
\end{aligned}$$

Using the expansion $\frac{1}{1+x}=1-x+x^2-x^3+\cdots$ with $x=\mathcal{O}(\lambda)$,

$$E_n-E_m^{(0)} = \left(E_n^{(0)}-E_m^{(0)}\right)\frac{1}{1-\mathcal{O}(\lambda)}$$

and plugging this in to (5) we get

$$\begin{aligned}\left\langle \psi_m^{(0)}|\psi_n\right\rangle &= \frac{\lambda\left\langle \psi_m^{(0)}\right| H'\left(\left|\psi_n^{(0)}\right\rangle + \lambda\left|\psi_n^{(1)}\right\rangle + \mathcal{O}(\lambda^2)\right)}{E_n^{(0)} - E_m^{(0)}}\left[1+\mathcal{O}(\lambda^2)\right] \\ &= \frac{\lambda\left\langle \psi_m^{(0)}\right| H'\left|\psi_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} + \mathcal{O}(\lambda^2), \qquad n \notin D_n. \end{aligned} \tag{6}$$

If instead $m \in D_n$ then

$$\begin{aligned} E_n - E_m^{(0)} &= \cancel{\left(E_n^{(0)} - E_m^{(0)}\right)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(1)} + \mathcal{O}(\lambda^3) \\ &= \lambda E_n^{(1)}\left(1 + \lambda\left[\frac{E_n^{(2)}}{E_n^{(1)}} + \mathcal{O}(\lambda)\right]\right) \end{aligned}$$

Again, we use the expansion $\frac{1}{1+x} = 1 - x + x^2 - x^3 + \cdots$, but now with $x = \lambda\left[\frac{E_n^{(2)}}{E_n^{(1)}} + \mathcal{O}(\lambda)\right]$. We get

$$E_n - E_m^{(0)} = \left(E_n^{(0)} - E_m^{(0)}\right) + \frac{\lambda E_n^{(1)}}{1 - \lambda\frac{E_n^{(2)}}{E_n^{(1)}} + \mathcal{O}(\lambda^2)}.$$

Plugging this in to (5) we get

$$\begin{aligned}\left\langle \psi_m^{(0)}|\psi_n\right\rangle &= \frac{\left\langle \psi_m^{(0)}\right| H'\left(\left|\psi_n^{(0)}\right\rangle + \lambda\left|\psi_n^{(1)}\right\rangle + \mathcal{O}(\lambda^2)\right)}{E_n^{(1)}}\left[1 - \lambda\frac{E_n^{(2)}}{E_n^{(1)}} + \mathcal{O}(\lambda^2)\right] \\ &= \frac{\left\langle \psi_m^{(0)}\right| H'\left|\psi_n^{(0)}\right\rangle}{E_n^{(1)}} + \lambda\left[\frac{\left\langle \psi_m^{(0)}\right| H'\left|\psi_n^{(1)}\right\rangle}{E_n^{(1)}} - \frac{E_n^{(2)}\left\langle \psi_m^{(0)}\right| H'\left|\psi_n^{(0)}\right\rangle}{\left[E_n^{(1)}\right]^2}\right] + \mathcal{O}(\lambda^2), \quad n \in D_n. \end{aligned} \tag{7}$$

Now, we can write an expression for complete state. We have $|\psi_n\rangle = \sum_m \left|\psi_m^{(0)}\right\rangle\left\langle \psi_m^{(0)}|\psi_n\right\rangle$ and we can read off the $\left\langle \psi_m^{(0)}|\psi_n\right\rangle$ from (6) and (7). Putting this all together,

$$\begin{aligned}\left|\psi_n^{(0)}\right\rangle + \lambda\left|\psi_n^{(1)}\right\rangle + \mathcal{O}(\lambda^2) &= \sum_{m\in D_n}\left|\psi_m^{(0)}\right\rangle\frac{\left\langle \psi_m^{(0)}\right| H'\left|\psi_n^{(0)}\right\rangle}{E_n^{(1)}} \\ &\quad + \lambda\left\{\sum_{m\in D_n}\left|\psi_m^{(0)}\right\rangle\left[\frac{\left\langle \psi_m^{(0)}\right| H'\left|\psi_n^{(1)}\right\rangle}{E_n^{(1)}} - \frac{E_n^{(2)}\left\langle \psi_m^{(0)}\right| H'\left|\psi_n^{(0)}\right\rangle}{\left[E_n^{(1)}\right]^2}\right]\right. \\ &\quad \left. + \sum_{m\notin D_n}\left|\psi_m^{(0)}\right\rangle\frac{\left\langle \psi_m^{(0)}\right| H'\left|\psi_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}}\right\} \\ &\quad + \mathcal{O}(\lambda^2). \end{aligned} \tag{8}$$

Equating orders of λ, we have a zero-order equation

$$\boxed{\left|\psi_n^{(0)}\right\rangle = \sum_{m\in D_n}\left|\psi_m^{(0)}\right\rangle\frac{\left\langle \psi_m^{(0)}\right| H'\left|\psi_n^{(0)}\right\rangle}{E_n^{(1)}}} \tag{9}$$

and a first-order equation

$$\boxed{\left|\psi_n^{(1)}\right\rangle = \sum_{m\in D_n}\left|\psi_m^{(0)}\right\rangle\left[\frac{\left\langle\psi_m^{(0)}\right|H'\left|\psi_n^{(1)}\right\rangle}{E_n^{(1)}} - \frac{E_n^{(2)}\left\langle\psi_m^{(0)}\right|H'\left|\psi_n^{(0)}\right\rangle}{\left[E_n^{(1)}\right]^2}\right] + \sum_{m\notin D_n}\left|\psi_m^{(0)}\right\rangle\frac{\left\langle\psi_m^{(0)}\right|H'\left|\psi_n^{(0)}\right\rangle}{E_n^{(0)}-E_m^{(0)}}.} \tag{10}$$

1(a).4 First order energy

Multiplying (9) by $\left\langle\psi_n^{(0)}\right|$,

$$\left\langle\psi_n^{(0)}|\psi_n^{(0)}\right\rangle = \sum_{m\in D_n}\left\langle\psi_n^{(0)}|\psi_m^{(0)}\right\rangle\frac{\left\langle\psi_m^{(0)}\right|H'\left|\psi_n^{(0)}\right\rangle}{E_n^{(1)}}$$

$$1 = \sum_{m\in D_n}\delta_{mn}\frac{\left\langle\psi_m^{(0)}\right|H'\left|\psi_n^{(0)}\right\rangle}{E_n^{(1)}}$$

so

$$\boxed{E_n^{(1)} = \left\langle\psi_n^{(0)}\right|H'\left|\psi_n^{(0)}\right\rangle}.$$

In words, the first order energy correction is the expectation value of H' for the zero-order state.

2 Identical particles

Suppose we have a system of two identical particles with the wavefunction $\Psi(x_1, x_2)$ where x_1 and x_2 are coordinates of the particles (taking into account things like position and spin).

Fact of Nature 1. *Particles either have wavefunctions that are symmetric, with $\Psi(x_1, x_2) = \Psi(x_2, x_1)$, or antisymmetric, with $\Psi(x_1, x_2) = -\Psi(x_2, x_1)$.*

We call the symmetric type of particles bosons and the antisymmetric type of particles fermions.

2(a) Pauli exclusion principle

Consider a wavefunction $\Psi(x_1, x_2)$ for two fermions. If $x_1 = x_2 = x$ then we have $\Psi(x, x) = -\Psi(x, x)$ so it must be that $\Psi(x, x) = 0$. This shows that two identical fermions cannot occupy the same state.