Lecture 24 (Dec. 4, 2017)

24.1   Non-degenerate Time-Independent Perturbation Theory

We now consider the problem of approximating the spectrum for a Hamiltonian of the form

$$H = H_0 + V \,, \tag{24.1}$$

where H_0 is a Hamiltonian with a known spectrum, and V is a "small" perturbation. This is the problem we began discussing in the last lecture. As a bookkeeping device, we introduced a parameter λ, and wrote

$$H = H_0 + \lambda V \,. \tag{24.2}$$

This parameter will allow us to organize our power counting analysis, and we can set $\lambda = 1$ at the end.

We have

$$H_0|n_0\rangle = E_{n,0}|n_0\rangle \,, \quad \langle m_0|n_0\rangle = \delta_{m_0,n_0} \,, \tag{24.3}$$

and we wish to solve

$$(H_0 + \lambda V)|n\rangle = E_n|n\rangle \,. \tag{24.4}$$

We expand the energy eigenstates of H in the form

$$|n\rangle = |n_0\rangle + \lambda|n_1\rangle + \lambda^2|n_2\rangle + \cdots \,, \tag{24.5}$$

and the corresponding energy eigenvalues in the form

$$E_n = E_{n,0} + \lambda E_{n,1} + \lambda^2 E_{n,2} + \cdots \,. \tag{24.6}$$

This gives us

$$(H_0 + \lambda V)(|n_0\rangle + \lambda|n_1\rangle + \cdots) = (E_{n,0} + \lambda E_{n,1} + \cdots)(|n_0\rangle + \lambda|n_1\rangle + \cdots) \,. \tag{24.7}$$

24.1.1   The First-Order Energy Shift

We can compare the two sides of Eq. (24.7) order-by-order in λ. At $O(\lambda^0)$, we get

$$H_0|n_0\rangle = E_{n,0}|n_0\rangle \,, \tag{24.8}$$

which we already knew. At $O(\lambda^1)$, we find

$$V|n_0\rangle + H_0|n_1\rangle = E_{n,0}|n_1\rangle + E_{n,1}|n_0\rangle \,. \tag{24.9}$$

If we take the inner product of this equation with $|n_0\rangle$, then we find

$$\langle n_0|V|n_0\rangle + \langle n_0|H_0|n_1\rangle = \langle n_0|E_{n,0}|n_1\rangle + E_{n,1} \,. \tag{24.10}$$

The second term on the left equals the first on the right, and so we are left with

$$E_{n,1} = \langle n_0|V|n_0\rangle \,. \tag{24.11}$$

This result makes sense, even classically: if we perturb the Hamiltonian, the leading-order shift in the energy of an eigenstate is just the expectation of the perturbation in the unperturbed eigenstate.

24.1.2   The First-Order Correction to the Eigenstate

Next we want to find $|n_1\rangle$, the leading-order correction to the energy eigenstate. Rearranging the $O(\lambda^1)$ terms of Eq. (24.7), we have

$$(H_0 - E_{n,0})|n_1\rangle = (E_{n,1} - V)|n_0\rangle. \qquad (24.12)$$

If we insert

$$\mathbb{1} = \sum_{m_0} |m_0\rangle\langle m_0| \qquad (24.13)$$

on both sides of this equation, the left-hand side becomes

$$(H_0 - E_{n,0})|n_1\rangle = \sum_{m_0}(H_0 - E_{n,0})|m_0\rangle\langle m_0|n_1\rangle = \sum_{m_0}(E_{m,0} - E_{n,0})|m_0\rangle\langle m_0|n_1\rangle, \qquad (24.14)$$

while the right-hand side becomes

$$(E_{n,1} - V)|n_0\rangle = \sum_{m_0}|m_0\rangle\langle m_0|(E_{n,1} - V)|n_0\rangle = \sum_{m_0}|m_0\rangle(E_{n,1}\langle m_0|n_0\rangle - \langle m_0|V|n_0\rangle). \qquad (24.15)$$

We now assert that we can choose $\langle n_0|n_1\rangle = 0$; you can check that this is possible by considering the normalization of $|n\rangle$. The left-hand side then becomes

$$(H_0 - E_{n,0})|n_1\rangle = \sum_{m_0 \neq n_0}(E_{m,0} - E_{n,0})|m_0\rangle\langle m_0|n_1\rangle, \qquad (24.16)$$

while the right-hand side becomes

$$(E_{n,1} - V)|n_0\rangle = \sum_{m_0}|m_0\rangle(\langle n_0|V|n_0\rangle\delta_{n_0 m_0} - \langle m_0|V|n_0\rangle) = -\sum_{m_0 \neq n_0}|m_0\rangle\langle m_0|V|n_0\rangle. \qquad (24.17)$$

Comparing these expressions, we find

$$|n_1\rangle = \sum_{m_0 \neq n_0} \frac{|m_0\rangle\langle m_0|V|n_0\rangle}{E_{n,0} - E_{m,0}}. \qquad (24.18)$$

Note that this expression only makes sense when the energy eigenvalues of H_0 are not degenerate.

We can now deduce a condition for the validity of perturbation theory: we demand that $\langle n_1|n_1\rangle \ll 1$ so that the first correction to the energy eigenstates is small, i.e., that

$$|\langle m_0|V|n_0\rangle| \ll |E_{n,0} - E_{m,0}| \qquad (24.19)$$

and that their ratio decreases rapidly enough with increasing m_0.

24.1.3   The Second-Order Energy Shift

Now, we are prepared to compute $E_{n,2}$, the second-order correction to the energy. At $O(\lambda^2)$ in Eq. (24.7), we have

$$H_0|n_2\rangle + V|n_1\rangle = E_{n,0}|n_2\rangle + E_{n,1}|n_1\rangle + E_{n,2}|n_0\rangle. \qquad (24.20)$$

If we take the inner product with $|n_0\rangle$, we can use

$$\langle n_0|H_0|n_2\rangle = E_{n,0}\langle n_0|n_2\rangle, \qquad (24.21)$$

to eliminate the first term from each side, leaving us with

$$\langle n_0|V|n_1\rangle = E_{n,1}\cancelto{0}{\langle n_0|n_1\rangle} + E_{n,2}\langle n_0|n_0\rangle. \tag{24.22}$$

Because $|n_0\rangle$ is normalized, this gives us

$$E_{n,2} = \langle n_0|V|n_1\rangle = \sum_{m_0\neq n_0} \frac{|\langle n_0|V|m_0\rangle|^2}{E_{n,0} - E_{m,0}}. \tag{24.23}$$

Again, this only makes sense if the energy eigenstates of H_0 are non-degenerate. To second order, we then have

$$E_n = E_{n,0} + \langle n_0|V|n_0\rangle + \sum_{m_0\neq n_0} \frac{|\langle n_0|V|m_0\rangle|^2}{E_{n,0} - E_{m,0}} + O(V^3). \tag{24.24}$$

24.2 Examples of Time-Independent Perturbation Theory

24.2.1 Spin in a Magnetic Field

Consider a spin-$\frac{1}{2}$ in a magnetic field of the form

$$\boldsymbol{B} = B_x\hat{\boldsymbol{x}} + B_0\hat{\boldsymbol{z}}, \tag{24.25}$$

with $B_x \ll B_0$ (assume that both B_x and B_0 are positive). The Hamiltonian is

$$H = -\gamma\boldsymbol{B}\cdot\boldsymbol{S} = -\gamma(B_0 S^z + B_x S^z) = -\gamma\frac{\hbar}{2}(B_0\sigma^z + B_x\sigma^x). \tag{24.26}$$

To analyze this system using perturbation theory, we define

$$H_0 = -\frac{\gamma\hbar}{2}B_0\sigma^z, \quad V = -\frac{\gamma\hbar}{2}B_x\sigma^x. \tag{24.27}$$

To zeroth order, the energy eigenstates are $|+\rangle$ with energy $-\gamma\hbar B_0/2$ and $|-\rangle$ with energy $+\gamma\hbar B_0/2$. To second order, the shift in the energy of the state $|+\rangle$ is

$$\begin{aligned}
\Delta E_+ &= \langle+|V|+\rangle + \frac{|\langle-|V|+\rangle|^2}{E_+ - E_-} \\
&= -\frac{\gamma\hbar B_x}{2}\cancelto{0}{\langle+|\sigma^x|+\rangle} + \left(\frac{\gamma\hbar B_x}{2}\right)^2\frac{|\langle-|\sigma^x|+\rangle|^2}{-\gamma\hbar B_0} \\
&= \frac{\gamma\hbar}{2}\left(-\frac{B_x^2}{2B_0}\right).
\end{aligned} \tag{24.28}$$

Similarly, we find

$$\Delta E_- = \frac{\gamma\hbar}{2}\left(\frac{B_x^2}{2B_0}\right). \tag{24.29}$$

Thus, the higher energy eigenvalue increases and the lower energy eigenvalue decreases. This is a general property of non-degenerate, time-independent perturbation theory: the second-order perturbation will always lower the energy of the ground state, because the numerator will be positive (as it is the sum of squares) and the denominator will be negative (as the ground state has lower energy than each other state).

We know the exact energy eigenvalues for this system are

$$\mp\frac{\gamma\hbar}{2}\sqrt{B_0^2 + B_x^2} \approx \mp\frac{\gamma\hbar}{2}B_0\left(1 + \frac{B_x^2}{2B_0^2} + \cdots\right) = \mp\frac{\gamma\hbar}{2}B_0 + \frac{\gamma\hbar}{2}\left(\mp\frac{B_x^2}{2B_0}\right) + O(B_x^3), \tag{24.30}$$

which exactly matches our calculation from perturbation theory.

24.2.2   The Quadratic Stark effect

Consider an atom in a weak uniform external electric field. What is the effect on the ground state energy? We will not worry about the issue of ionization, as the likelihood of ionization from applying a small electric field is very small. Thus, we ignore the possibility that the electron can escape from the atom.

We take the unperturbed Hamiltonian to be

$$H_0 = \frac{p^2}{2m} + V_0(r) \,, \tag{24.31}$$

With V_0 rotationally symmetric, e.g.

$$V_0 = -\frac{e^2}{r} \tag{24.32}$$

for the hydrogen atom. We then take the perturbing Hamiltonian to be

$$V = -eEz \,, \tag{24.33}$$

where we have simply defined the z-axis to be the one pointing in the direction of the electric field.

The energy shift of the ground state is then

$$\Delta E_0 = \langle 0|V|0 \rangle + \sum_{n \neq 0} \frac{|\langle n|V|0 \rangle|^2}{E_0 - E_n} + \cdots . \tag{24.34}$$

The first term vanishes by symmetry arguments, using either parity or rotational symmetry. Thus, the shift starts at second order. We then have

$$\Delta E_0 = e^2 E^2 \sum_{n \neq 0} \frac{|\langle n|z|0 \rangle|^2}{E_0 - E_n} + \cdots . \tag{24.35}$$

The second-order term is negative. We define α, called the *atomic polarizability*, such that

$$\Delta E_0 = -\frac{1}{2}\alpha E^2 + \cdots . \tag{24.36}$$

We could have written this form down simply by symmetry arguments, but now we have a way to calculate its value:

$$\alpha = 2e^2 \sum_{n \neq 0} \frac{|\langle n|z|0 \rangle|^2}{E_n - E_0} \,. \tag{24.37}$$

In order to proceed further, we need to know the particular value of $V_0(r)$ for the system we are trying to solve. For the hydrogen atom, it turns out that this calculation can be done exactly. Dimensional analysis gives us most of the answer: we have

$$\alpha \sim e^2 \frac{\text{length}^2}{\text{energy}} \,. \tag{24.38}$$

The only length scale in the hydrogen atom is the Bohr radius a_0, and the only energy scale is e^2/a_0, which is a Rydberg. Thus, we have

$$\alpha \sim \frac{e^2 a_0^2}{e^2/a_0} \sim a_0^3 \,. \tag{24.39}$$

For hydrogen, the exact answer turns out to be

$$\alpha = 4.5 a_0^3 \,. \tag{24.40}$$

24.2.3　Van der Waals Interaction

An important interaction in chemistry and biology is the van der Waals force. Given two (hydrogen) atoms in their respective ground states, separated by a distance $r \gg a_0$ (with a_0 the Bohr radius), how does the total ground state energy depend on r?

Take the direction of separation to be the z-direction. We will take the two protons to be fixed in position. The full Hamiltonian is

$$
\begin{aligned}
H &= H_0 + H_1\,, \\
H_0 &= -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{r_1} - \frac{e^2}{r_2}\,, \\
H_1 &= \frac{e^2}{r} + \frac{e^2}{|\boldsymbol{r} + \boldsymbol{r}_2 - \boldsymbol{r}_1|} - \frac{e^2}{|\boldsymbol{r} + \boldsymbol{r}_2|} - \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}_1|}\,,
\end{aligned}
\tag{24.41}
$$

where $\boldsymbol{r}$ is the vector separating the protons, and $\boldsymbol{r}_i$ are the vectors separating the electrons from their respective protons.

If $r \gg a_0$, then we can expand H_1 in powers of $\boldsymbol{r}_i/r$. This is a multipole expansion. The leading term in this case is a dipole–dipole interaction,

$$
\begin{aligned}
H_1 &= \frac{e^2}{r^3}(x_1 x_2 + y_1 y_2 - 2z_1 z_2) + O\left(\frac{1}{r^4}\right) \\
&= \frac{e^2}{r^3}(\boldsymbol{r}_1 \cdot \boldsymbol{r}_2 - 3(\boldsymbol{r}_1 \cdot \hat{\boldsymbol{r}})(\boldsymbol{r}_2 \cdot \hat{\boldsymbol{r}})) + O\left(\frac{1}{r^4}\right).
\end{aligned}
\tag{24.42}
$$

We then perturb in H_1. The zeroth order ground state is

$$
\psi_{\mathrm{gd}} = \psi_{\mathrm{gd}}^1(\boldsymbol{r}_1)\psi_{\mathrm{gd}}^2(\boldsymbol{r}_2)\,.
\tag{24.43}
$$

We then have

$$
\begin{aligned}
\Delta E^{(1)} &= \langle \mathrm{gd}|H_1(\boldsymbol{r}_1, \boldsymbol{r}_2)|\mathrm{gd}\rangle \\
&= e^2\langle \mathrm{gd}|\frac{x_1 x_2 + y_1 y_2 - 2z_1 z_2}{r^3}|\mathrm{gd}\rangle\,.
\end{aligned}
\tag{24.44}
$$

Note that

$$
\langle \mathrm{gd}|x_1 x_2|\mathrm{gd}\rangle = \langle (\mathrm{gd})_1|x_1|(\mathrm{gd})_1\rangle\langle (\mathrm{gd})_2|x_2|(\mathrm{gd})_2\rangle = 0\,,
\tag{24.45}
$$

and similarly for all terms in $\Delta E^{(1)}$. Thus, the leading-order energy shift comes in at second order.

We find

$$
\Delta E^{(2)} = \frac{e^4}{r^6}\sum_{k \neq 0}\frac{|\langle k_1, k_2|x_1 x_2 + y_1 y_2 - 2z_1 z_2|0, 0\rangle|^2}{E_{0,0} - E_{k_1,k_2}}\,.
\tag{24.46}
$$

Dimensional analysis tells us that

$$
\Delta E^{(2)} \sim -\frac{e^4}{r^6}\frac{a_0^4}{\mathrm{Ry}} \sim -\frac{e^2 a_0^5}{r^6}\,,
\tag{24.47}
$$

where the Rydberg is e^2/a_0. The punchline is that there is a weak attractive interaction, which is the van der Waals interaction. This is a purely quantum mechanical effect, arising because the dipole–dipole interaction induces virtual transitions to the excited states in each atom.

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