

Perturbative Methods

1 Time Independent Perturbation Theory

The number of exactly soluble problems in quantum mechanics (and hence the number of exactly soluble propagators) is limited to the familiar cases

- i) Free particle
- ii) Harmonic oscillator
- iii) Hydrogen atom
- iv) $\cosh^{-2} ax$ potential, *etc.*

known from elementary quantum texts. For application to realistic situations we require a technique which is applicable to a more general class of problems. A common case is that wherein the full Hamiltonian \hat{H} can be separated into two components — \hat{H}_0 for which exact solutions are available and \hat{H}' which is in some sense small — *e.g.*

$$\frac{\langle \phi | \hat{H}' | \psi \rangle}{\langle \phi | \hat{H}^{(0)} | \psi \rangle} \ll 1 \quad (1)$$

with \hat{H}' being time independent. In this case one can use the methods of time independent perturbation theory, which we now develop.

2 Time Independent Perturbation Theory

Suppose the problem to be solved is of the form

$$\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle \quad (2)$$

subject to some boundary conditions. Suppose further that one is able to solve the related problem

$$\hat{H}^{(0)} |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle \quad (3)$$

where \hat{H} differs from $\hat{H}^{(0)}$ by some small interaction term \hat{H}'

$$\hat{H} = \hat{H}^{(0)} + \hat{H}' \quad (4)$$

Correspondingly let $|\psi\rangle = |\psi_n^{(0)}\rangle + |\psi'_n\rangle$, where both $|\psi_n\rangle$ and $|\psi_n^{(0)}\rangle$ are normalized to unity, and $E_n = E_n^{(0)} + E'_n$. The quantities $E'_n, |\psi'_n\rangle$ are then perturbations of $E_n, |\psi_n\rangle$ due to the presence of \hat{H}' . We have then

$$(\hat{H}^{(0)} + \hat{H}')(|\psi_n^{(0)}\rangle + |\psi'_n\rangle) = (E_n^{(0)} + E'_n)(|\psi_n^{(0)}\rangle + |\psi'_n\rangle) \quad (5)$$

or, rearranging,

$$0 = (\hat{H}^{(0)} - E_n^{(0)})|\psi_n^{(0)}\rangle + (\hat{H}^{(0)} - E_n^{(0)})|\psi'_n\rangle + (\hat{H}' - E'_n)|\psi'_n\rangle \quad (6)$$

The first term vanishes, since $|\psi_n^{(0)}\rangle$ is an eigenstate of $\hat{H}_n^{(0)}$ with eigenvalue $E_n^{(0)}$. Now take the inner product with $\langle\psi_n^{(0)}|$, which yields

$$0 = \langle\psi_n^{(0)}|\hat{H}^{(0)} - E_n^{(0)}|\psi'_n\rangle + \langle\psi_n^{(0)}|\hat{H}' - E'_n|\psi_n\rangle \quad (7)$$

Again the first term vanishes, since $\hat{H}^{(0)}$ is hermitian, and we are left with

$$E'_n = \frac{\langle\psi_n^{(0)}|\hat{H}'|\psi_n\rangle}{\langle\psi_n^{(0)}|\psi_n\rangle} \quad (8)$$

As it stands, the utility of this result appears dubious, since we do not know the exact solutions $|\psi_n\rangle$. However, we shall show how to handle this situation.

We write $\hat{H}' = \lambda\hat{H}^{(1)}$, where λ is a small (real) parameter. Now expand in terms of λ —

$$\begin{aligned} |\psi_n\rangle &= |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots \\ E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \end{aligned} \quad (9)$$

Then we have

$$\lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots = \frac{\lambda \langle\psi_n^{(0)}|\hat{H}^{(1)}|\psi_n^{(0)}\rangle + \lambda^2 \langle\psi_n^{(0)}|\hat{H}^{(1)}|\psi_n^{(1)}\rangle + \dots}{\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle + \lambda \langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + \dots} \quad (10)$$

Since this equation must be valid for arbitrary λ we can equate the coefficients of powers of λ on both sides, yielding

$$\begin{aligned} E_n^{(1)} &= \langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle \\ E_n^{(2)} &= \langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(1)} \rangle - \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle E_n^{(1)} \\ E_n^{(3)} &= \dots \end{aligned} \quad (11)$$

The expression for $E_n^{(2)}$ can be simplified if we note that

$$1 = \langle \psi_n | \psi_n \rangle = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + \lambda \left[\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle \right] + \dots \quad (12)$$

Hence $\text{Re} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$ and, since $E_n^{(2)}$ is real,

$$E_n^{(2)} = \text{Re} \langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(1)} \rangle \quad (13)$$

Usually one chooses $|\psi_n^{(1)}\rangle$ to be orthogonal to $|\psi_n^{(0)}\rangle$ so that $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$. Then $E_n^{(2)} = \langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(1)} \rangle$.

In order to evaluate $|\psi_n^{(1)}\rangle$ we expand in terms of unperturbed eigenstates

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n} |c_m \psi_m^{(0)}\rangle \quad (14)$$

where there is no term with $m = n$ in the sum, due to the assumed orthogonality. Now

$$(\hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \dots)(|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \dots) = (E_n^{(0)} + \lambda E_n^{(1)} + \dots)(|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \dots) \quad (15)$$

Equating terms in λ yields

$$\begin{aligned} \hat{H}^{(0)} |\psi_n^{(1)}\rangle + \hat{H}^{(1)} |\psi_n^{(0)}\rangle &= E_n^{(0)} |\psi_n^{(1)}\rangle + E_n^{(1)} |\psi_n^{(0)}\rangle \\ \sum_{m \neq n} (E_m^{(0)} - E_n^{(0)}) c_m |\psi_m^{(0)}\rangle &= (E_n^{(1)} - \hat{H}^{(1)}) |\psi_n^{(0)}\rangle \end{aligned} \quad (16)$$

If we take the inner product with $\langle \psi_n^{(0)} |$, we find the already obtained result

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle \quad (17)$$

However, if we take the inner product with $\langle \psi_m^{(0)} |$, where $m \neq n$, we find

$$c_m = \frac{\langle \psi_m^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \quad (18)$$

This yields the first order wavefunction shift

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n} \frac{|\psi_m^{(0)}\rangle \langle \psi_m^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \quad (19)$$

and the second order energy shift

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \quad (20)$$

Finally, now that λ has performed its purpose of separating out appropriate orders, we let $\lambda = 1$ so that $\hat{H}^{(1)} = \hat{H}'$. In principle one could now continue to higher orders, but generally one stops here.

Now consider an example, in order to show the utility of the procedure. Consider a harmonic oscillator with spring constant K and mass m . The energy levels are then given by

$$E_n^{(0)} = n + \frac{1}{2}\omega_0 \quad \text{with} \quad \omega_0 = \sqrt{\frac{K}{m}} \quad (21)$$

Now include alongside an additional spring with spring constant b . By how much are the energy levels changed? Of course, we know how to solve this problem exactly—the new energy levels are given by

$$E_n^{(0)} = (n + \frac{1}{2})\omega \quad \text{with} \quad \omega = \sqrt{\frac{K+b}{m}} = \omega_0 \sqrt{1 + \frac{b}{K}} \simeq \omega_0 \left(1 + \frac{1}{2} \frac{b}{K} + \dots\right) \quad (22)$$

but it is also useful to attack this problem perturbatively. For the first order energy shift we have

$$\begin{aligned} E_n^{(1)} &= \frac{b}{2} \langle \psi_n^{(0)} | \hat{x}^2 | \psi_n^{(0)} \rangle \\ &= \frac{b}{4m\omega_0} \langle \psi_n^{(0)} | (\hat{a} + \hat{a}^\dagger)(\hat{a} + \hat{a}^\dagger) | \psi_n^{(0)} \rangle \\ &= \frac{b}{2m\omega_0} \langle \psi_n^{(0)} | \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} | \psi_n^{(0)} \rangle = \frac{b}{2m\omega_0} (2n+1) \\ &= \frac{b}{2K} \omega_0 (n + \frac{1}{2}) \end{aligned} \quad (23)$$

in agreement with the expansion of the exact result. Similarly the higher order shifts can be shown to agree.

3 Degenerate TIPT

Suppose that in the absence of the perturbation, the system has states which are degenerate in energy. Consider, *e.g.*, a two-state system wherein $|\psi_1^{(0)}\rangle$ and $|\psi_2^{(0)}\rangle$ are an orthogonal pair of unperturbed states corresponding to energy $E^{(0)}$. Because of the degeneracy, when the perturbation is turned on the perturbed state may be very different from the unperturbed one. (This is in fact suggested by Eq. 18 since the states are degenerate.) However, we assume that there exists some linear combination

$$|\psi^{(0)}\rangle = c_1|\psi_1^{(0)}\rangle + c_2|\psi_2^{(0)}\rangle \quad (24)$$

from which the exact eigenfunction differs only slightly. Then we write

$$(\hat{H}^{(0)} + \hat{H}^{(1)})(|\psi^{(0)}\rangle + |\psi^{(1)}\rangle) = (E^{(0)} + E^{(1)})(|\psi^{(0)}\rangle + |\psi^{(1)}\rangle) \quad (25)$$

Neglecting second order terms

$$\begin{aligned} & (\hat{H}^{(0)} - E^{(0)})|\psi^{(1)}\rangle + (\hat{H}^{(1)} - E^{(1)})|\psi^{(0)}\rangle = 0 \\ & = (\hat{H}^{(0)} - E^{(0)})|\psi^{(1)}\rangle + (\hat{H}^{(1)} - E^{(1)})(c_1|\psi_1^{(0)}\rangle + c_2|\psi_2^{(0)}\rangle) \end{aligned} \quad (26)$$

Taking the inner product with $\langle\psi_1^{(0)}|$, $\langle\psi_2^{(0)}|$ and defining the effective 2×2 Hamiltonian

$$H_{ij} = H_{ji}^* = \langle\psi_i^{(0)}|\psi_j^{(0)}\rangle \quad (27)$$

we have

$$\begin{aligned} c_1(H_{11} - E^{(1)}) + c_2H_{12} &= 0 \\ c_1H_{21} + c_2(H_{22} - E^{(1)}) &= 0 \end{aligned} \quad (28)$$

which is simply the diagonalization condition for the effective Hamiltonian H_{ij} . Eqs. 28 are compatible only if

$$\frac{c_1}{c_2} = -\frac{H_{12}}{H_{11} - E^{(1)}} = -\frac{H_{22} - E^{(1)}}{H_{21}} \quad (29)$$

Thus

$$(H_{11} - E^{(1)})(H_{22} - E^{(1)}) - |H_{12}|^2 = 0 \quad (30)$$

whose solution is

$$E^{(1)} = \frac{1}{2} \left[(H_{11} + H_{22}) \pm \sqrt{(H_{11} - H_{22})^2 + 4|H_{12}|^2} \right] \quad (31)$$

Hence the degeneracy is removed unless $H_{ij} = 0$.

As an example, consider the effect of an electric field on the energy levels of the hydrogen atom. For simplicity we consider its effect on the $n = 1$ and $n = 2$ levels. Choose the field to be $\vec{E} = E_0 \hat{e}_z$ and the perturbing Hamiltonian to be $H^{(1)} = -eE_0 z$. Since the ground state $|\psi_{100}\rangle$ is nondegenerate, we find simply

$$E_{100}^{(1)} = \langle \psi_{100} | \hat{H}^{(1)} | \psi_{100} \rangle = 0 \quad (32)$$

since $\int d^3r |\psi_{100}(\vec{r})|^2 z = 0$. On the other hand, for the $n = 2$ levels, we have quadruply degenerate states $|\psi_{211}\rangle, |\psi_{210}\rangle, |\psi_{21-1}\rangle, |\psi_{200}\rangle$. Now define

$$|1\rangle = |\psi_{211}\rangle, \quad |2\rangle = |\psi_{210}\rangle, \quad |3\rangle = |\psi_{21-1}\rangle, \quad |4\rangle = |\psi_{200}\rangle \quad (33)$$

and calculate matrix elements $H_{ij} = \langle i | \hat{H}^{(1)} | j \rangle$. As before we assume the existence of definite energy eigenstates which are only slightly different from linear combinations of the states $|i\rangle$:

$$(\hat{H}^{(0)} + \hat{H}^{(1)})(|\psi^{(0)}\rangle + |\psi^{(1)}\rangle) = (E^{(0)} + E^{(1)})(|\psi^{(0)}\rangle + |\psi^{(1)}\rangle) \quad (34)$$

where $|\psi^{(0)}\rangle = \sum_i c_i |i\rangle$. Taking inner products with $\langle j|$ we find the set of equations

$$\begin{aligned} c_1(H_{11} - E^{(1)}) + c_2 H_{12} + c_3 H_{13} + c_4 H_{14} &= 0 \\ c_1 H_{21} + c_2(H_{22} - E^{(1)}) + c_3 H_{23} + c_4 H_{24} &= 0 \\ c_1 H_{31} + c_2 H_{32} + c_3(H_{33} - E^{(1)}) + c_4 H_{34} &= 0 \\ c_1 H_{41} + c_2 H_{42} + c_3 H_{43} + c_4(H_{44} - E^{(1)}) &= 0 \end{aligned} \quad (35)$$

This set of equations has a solution if and only if

$$\det \begin{pmatrix} H_{11} - E^{(1)} & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} - E^{(1)} & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} - E^{(1)} & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} - E^{(1)} \end{pmatrix} = 0 \quad (36)$$

For the case at hand we find that the diagonal elements vanish

$$H_{ii} = \langle i | \hat{H}^{(1)} | i \rangle = 0 \quad (37)$$

because the integrand is an odd function of z . For the off-diagonal elements we note that $[L_z, z] = 0$. Hence

$$0 = \langle i | [L_z, z] | j \rangle = (m_i - m_j) H_{ij} \quad (38)$$

Thus $H_{ij} = 0$ unless $m_i = m_j$, which means that the only nonvanishing elements of H_{ij} are $H_{24} = H_{42}^*$, with

$$\begin{aligned} H_{24} &= - \int d^3r R_{21}^*(r) Y_1^{0*}(\theta, \phi) e E_0 z R_{20}(r) Y_0^0(\theta, \phi) \\ &= - \frac{e E_0}{\sqrt{3}} \int d\Omega Y_1^{0*}(\theta, \phi) Y_1^0(\theta, \phi) \int_0^\infty dr r^3 R_{21}(r) R_{20}(r) \end{aligned} \quad (39)$$

Using

$$\begin{aligned} R_{20}(r) &= \frac{1}{2\sqrt{2}a_0^{\frac{3}{2}}} \left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{r}{2a_0}\right) \\ R_{21}(r) &= \frac{1}{2\sqrt{6}a_0^{\frac{3}{2}}} \frac{r}{a_0} \exp\left(-\frac{r}{2a_0}\right) \end{aligned} \quad (40)$$

where $a_0 = 1/m\alpha$ is the Bohr radius, we have

$$H_{24} = - \frac{e E_0}{24a_0^3} \int_0^\infty r^3 dr \frac{r}{a_0} \left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{r}{a_0}\right) = 3e E_0 a_0 \quad (41)$$

Thus we require

$$0 = \det \begin{pmatrix} -E^{(1)} & 0 & 0 & 0 \\ 0 & -E^{(1)} & 0 & 3e E_0 a_0 \\ 0 & 0 & -E^{(1)} & 0 \\ 0 & 3e E_0 a_0 & 0 & -E^{(1)} \end{pmatrix} = (E^{(1)})^4 - (3e E_0 a_0)^2 (E^{(1)})^2 \quad (42)$$

whose solutions are $E^{(1)} = 0, 0, 3e E_0 a_0, -3e E_0 a_0$. Solving for the eigenstates, we have

$$E^{(1)} = 0 \quad c_1 = 1 \quad c_2 = c_3 = c_4 = 0$$

$$\begin{aligned}
E^{(1)} &= 0 & c_3 &= 0 & c_1 &= c_2 = c_4 = 0 \\
E^{(1)} &= 3eE_0a_0 & c_1 &= c_3 = 0 & c_2 &= c_4 = \sqrt{\frac{1}{2}} \\
E^{(1)} &= -3eE_0a_0 & c_1 &= c_3 = 0 & c_2 &= -c_4 = \sqrt{\frac{1}{2}}
\end{aligned} \tag{43}$$

Thus we have

$$\begin{aligned}
E_+^{(1)} &= 3eE_0a_0 & |\psi_+^{(0)}\rangle &= \sqrt{\frac{1}{2}}(|\psi_{210}\rangle + |\psi_{200}\rangle) \\
E_-^{(1)} &= -3eE_0a_0 & |\psi_-^{(0)}\rangle &= \sqrt{\frac{1}{2}}(|\psi_{210}\rangle - |\psi_{200}\rangle)
\end{aligned} \tag{44}$$

Recalling that the energy associated with an electric dipole placed in an electric field is $U = -\vec{p} \cdot \vec{E}$, where \vec{p} is the electric dipole moment, we see that these eigenstates have a permanent dipole moment of magnitude $\vec{p} = \pm 3ea_0\hat{e}_z$, corresponding to the feature that the electron charge density is no longer centered on the proton.