Lecture 13

Feynman–Hellmann Theorem

Assume

\[ H(\alpha) |\psi(\alpha)\rangle = E(\alpha) |\psi(\alpha)\rangle \]

where \( \alpha \) represents parameters that appear in the Hamiltonian. Then

\[ \langle \psi(\alpha) | \frac{\partial H(\alpha)}{\partial \alpha} | \psi(\alpha) \rangle = \]

\[ \frac{\partial E(\alpha)}{\partial \alpha} \langle \psi(\alpha) | \psi(\alpha) \rangle \]

If \( \langle \psi(\alpha) | \psi(\alpha) \rangle = 1 \) then

\[ \langle \psi(\alpha) | \frac{\partial H(\alpha)}{\partial \alpha} | \psi(\alpha) \rangle = \frac{\partial E(\alpha)}{\partial \alpha} \]

Proof:

\[ \frac{d}{d\alpha} \langle \psi(\alpha) | H(\alpha) - E(\alpha) | \psi(\alpha) \rangle = 0 \]
using the chain rule

\[ \frac{\partial}{\partial \alpha_i} \left( \langle \Psi(\alpha) | (H(\alpha) - E(\alpha)) | \Psi(\alpha) \rangle \right) + \]

\[ \langle \Psi(\alpha) | \left( \frac{\partial H(\alpha)}{\partial \alpha_i} - \frac{\partial E(\alpha)}{\partial \alpha_i} \right) | \Psi(\alpha) \rangle + \]

\[ \left( \langle \frac{\partial \Psi(\alpha)}{\partial \alpha_i} | (H(\alpha) - E(\alpha)) | \Psi(\alpha) \rangle \right)^{**} \]

Thus as long as \( H(\alpha) = H(\alpha) \)

and \( | \Psi(\alpha) \rangle \) is an eigenstate

of \( H(\alpha) \) with eigenvalue \( E(\alpha) \),

the only remaining term

is the middle term

\[ \langle \Psi(\alpha) | \frac{\partial H(\alpha)}{\partial \alpha_i} | \Psi(\alpha) \rangle = \frac{\partial E(\alpha)}{\partial \alpha_i} \langle \Psi(\alpha) | \Psi(\alpha) \rangle \]

This completes the proof of the theorem.
example

\[ H = \frac{p^2}{2m} - \frac{ze^2}{r} \]

\[ = -\frac{\hbar^2}{2m} \nabla^2 - \frac{ze^2}{r} \]

\[ = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\ell(\ell+1)}{r^2} \right) - \frac{ze^2}{r} \]

\[ E(\ell) = -\frac{z^2e^4m}{2\hbar^2}(\ell + \ell + 1)^2 \]

we can use any of the above forms of the Hamiltonian

(1) compute \( \langle \psi(x) | p^2 | \psi(x) \rangle \)

\[ \frac{\hbar^2}{2m} = -\frac{p^2}{2m^2} \quad p^2 = -2m^2 \frac{\partial^2}{\partial \psi^2} \]

\[ \langle \psi | p^3 \rangle \psi = -2m^2 \langle \psi | \frac{\partial^2 \psi}{\partial \psi^2} \rangle \psi \]

\[ = -2m^2 \frac{\partial E}{\partial \psi} = (-2m^2) \left( -\frac{ze^2}{2\hbar^2} \right) \left( \frac{1}{(n+\ell+1)^2} \right) \]

\[ = \frac{z^2m^2e^4}{\hbar^2} \left( \frac{1}{(n+\ell+1)} \right)^2 \]
\[ \frac{\partial H}{\partial z} = -\frac{e^2}{r} \]

\[ -z \frac{\partial H}{\partial z} = -\frac{Z e^2}{r} = U \]

\[ \langle \Phi | U | \Phi \rangle = Z \langle \Phi | \left( -\frac{e^2}{r} \right) | \Phi \rangle = \]

\[ Z \frac{\partial E}{\partial z} = \frac{2 Z e^2 q}{2 \hbar^2} \left( \frac{1}{n + l + m} \right)^2 \]

* compute \( \langle \Phi | \frac{1}{r^2} | \Phi \rangle \)

\[ \frac{\partial H}{\partial z} = -\frac{\hbar^2}{2m} \left( -\frac{2e+1}{r^2} \right) \]

\[ \langle \Phi | \frac{1}{r^2} | \Phi \rangle = \frac{2m}{\hbar^2} \left( \frac{1}{2e+1} \right) \langle \Phi | \frac{\partial H}{\partial z} | \Phi \rangle \]

\[ \frac{2m}{\hbar^2} \left( \frac{1}{2e+1} \right) \left( -\frac{Z e^2 q}{2 \hbar^2} \right) \left( -2 \right) \left( \frac{1}{n+1+n+1} \right)^3 \]

\[ \frac{2m^2 Z e^2 q}{\hbar^4} \frac{1}{(2e+1)} \left( \frac{1}{n+e+1} \right)^3 \]
Another similar theorem is called the Virial Theorem. This theorem relates to the expectation value of the kinetic and potential energy in eigenstates of the Hamiltonian for potentials of the form

\[ V(r) = \alpha r^n \]

Consider

\[ H = -\frac{\hbar^2}{2m} \nabla^2 + \alpha r^n \]

\[ [\vec{p}, H] = -i\alpha \hbar \vec{V}(r) \]

for the Hamiltonian above.
\[ \mathcal{E}_1 \mu_1 = \frac{1}{2m} \mathcal{E}_1 \mu_2 = \frac{i \hbar}{2m} \cdot \mathbf{p} \]

Putting these together gives

\[ \begin{aligned} [\mathbf{p}, \mathcal{E}_1] &= -i \alpha \hbar \mathbf{r} \cdot \nabla \left( r^\alpha \right) + \frac{2 \alpha \hbar}{2m} \mathbf{p} \cdot \mathbf{p} \\ &= i \hbar \left( -\alpha \mathbf{r}^\alpha + \frac{\mathbf{p}^2}{m} \right) \end{aligned} \]

evaluating this commutator in eigenstate of \( \mathcal{H} \) gives

\[ \begin{aligned} 0 &= (\mathcal{E} - \mathcal{E}) \langle \psi | \mathbf{p} \cdot \mathbf{r} | \psi \rangle \\ &= i \hbar \left( -\alpha \mathbf{r}^\alpha + \frac{\mathbf{p}^2}{m} \right) \end{aligned} \]

canceling the \( i \hbar \) and using

\[ \begin{aligned} V &= \alpha \mathbf{r}^\alpha \\ T &= K \mathcal{E} = \frac{\mathbf{p}^2}{2m} \end{aligned} \]

this becomes

\[ \begin{aligned} 0 &= -\alpha \langle \psi | (V + T) | \psi \rangle + 2 \langle \psi | T | \psi \rangle \\ 2 \langle \psi | T | \psi \rangle &= \alpha \langle \psi | (V + T) | \psi \rangle \]

\[ 2 \langle \psi | T | \psi \rangle = \alpha \langle \psi | (V + T) | \psi \rangle \]
This can be combined with energy conservation:

\[ \langle \psi_{11114} \rangle = E = \langle \psi_{1114} \rangle + \frac{2}{n} \langle \psi_{1114} \rangle \]

\[ 2 \langle \psi_{1114} \rangle = n \langle \psi_{1114} \rangle \]

This can be used to express the expectation value of \( T \) or \( U \) in terms of the energy eigenvalue \( E \):

\[ E = \langle \psi_{1114} \rangle + \frac{2}{n} \langle \psi_{1114} \rangle \]

\[ = \left( 1 + \frac{2}{n} \right) \langle \psi_{1114} \rangle \]

\[ \langle \psi_{1114} \rangle = \left( \frac{n}{n+2} \right) E \]

\[ E = \frac{n}{2} \langle \psi_{1114} \rangle + \langle \psi_{1114} \rangle \]

\[ = \left( 1 + \frac{n}{2} \right) \langle \psi_{1114} \rangle \]

\[ \langle \psi_{1114} \rangle = \frac{2}{n+2} \ E \]
For \( n = -1 \) (one electron atom)

\[
\langle \Phi_1 \Phi_1 \rangle = 2E = -2 \langle \Phi_1 \Phi_1 \rangle
\]

\[
= -\frac{2e^4 m}{\hbar^2} \frac{1}{(n+e+1)^2}
\]

which agrees with the result of using the Hellmann–Feynman theorem.

The advantage of both of these theorems is that the results do not require performing an integration – they give useful information on the energy is distributed in terms of potential and kinetic terms.
Rayleigh–Schrödinger perturbation theory

Assume

\[ H = H_0 + V \]

where \( H_0 \) is simple to solve and \( V \) is "small".

Rayleigh–Schrödinger perturbation theory constructs solutions to the eigenvalue problem

\[ H |\psi\rangle = E |\psi\rangle \]

starting with solutions of

\[ H_0 |\psi^0\rangle = E^0 |\psi^0\rangle \]

and constructing correction is powers of the small interaction \( V \).
In order to keep track of powers of \( V \) we replace \( H \) by

\[
H(\lambda) = H_0 + \lambda V
\]

(eventually we will let \( \lambda \to 1 \))

the starting approximation is

the unperturbed solution

\[
H_0 |\psi_n^0 \rangle = E_n^0 |\psi_n^0 \rangle
\]

where we can choose the \( |\psi_n^0 \rangle \) for different \( n \) to be orthogonal. Next we assume the solutions to

\[
H |\psi_n \rangle = E_n |\psi_n \rangle
\]

can be represented as

a series in powers of \( V \)
\begin{align*}
|\Psi_n\rangle &= |\Psi_n^0\rangle + \sum_{m=1}^{\infty} \lambda^m |\Psi_n^m\rangle \\
E_n = E_n^0 + \sum_{m=1}^{\infty} \lambda^m E_n^m
\end{align*}

Substituting these expansions in the Schrödinger equation gives

\begin{align*}
H_0 \sum_{m=0}^{\infty} \lambda^m |\Psi_n^m\rangle + \sqrt{2} \sum_{m=0}^{\infty} \lambda^{m+1} |\Psi_n^{m+1}\rangle &= \sum_{r=0}^{\infty} \sum_{p=0}^{\infty} \lambda^r |\Psi_n^r\rangle |E_n^p\rangle \\
\sum_{r=0}^{\infty} \sum_{p=0}^{\infty} \lambda^r |\Psi_n^r\rangle |E_n^p\rangle &= E_n^p
\end{align*}

In the second term let \( m' = m+1 \) and in the third term let \( m = k+r \)

\begin{align*}
H_0 \sum_{m=0}^{\infty} \lambda^m |\Psi_n^m\rangle + \sqrt{2} \sum_{m'=1}^{\infty} \lambda^{m'} |\Psi_n^{m'}\rangle &= \sum_{m=0}^{\infty} \sum_{k=0}^{\infty} \lambda^k |\Psi_n^k\rangle |E_n^{m-k}\rangle \\
\sum_{m=0}^{\infty} \sum_{k=0}^{\infty} \lambda^k |\Psi_n^k\rangle |E_n^{m-k}\rangle &= E_n^{m-k}
\end{align*}

equating equal powers of \( \lambda \) gives the following relations
\[ H_0 \left\{ \psi_{m=0} \right\} = E_{m=0} \left\{ \psi_{m=0} \right\} \]

\[ H_0 1\psi_{m=0} > + \sqrt{V} 1\psi_{m=0} > = E_{m=0} \]

\[ \sum_{k=0}^{m-1} 1\psi_{m=0} > = E_{m} \]

The \( m=0 \) equation is satisfied by assumption. It is useful to write the second equation in the form:

\[ (H_0 - E_m) 1\psi_{m=0} > - 1\psi_{m=0} > E^m_m = \]

\[ - \sqrt{V} 1\psi_{m-1} > + \sum_{k=1}^{m-1} 1\psi_{m-k} > E_{m-k} \]

all of the terms on the right side of this equation involve \( 1\psi_k > E^k_k \) for \( k < m \).
(1) If \( \Psi_n^m \) is a solution to the equation on the last page, so is
\[ \Psi_n^m + \alpha \Psi_n^0 \]
where \( \alpha \) is an arbitrary constant.

This ambiguity can be avoided by requiring
\[ \langle \Psi_n^m | \Psi_n^0 \rangle = 0 \quad \text{all } m > 0 \]

(2) With this assumption,
\[ \Psi_n^0 = \Psi_n^0 + \sum_{m=1}^{\infty} \frac{\alpha^m}{m!} \Psi_n^m \]

both \( \Psi_n^m \) and \( \Psi_n^0 \) cannot both be normalized to 1 unless
\[ \sum_{m=1}^{\infty} \frac{\alpha^m}{m!} \| = 0 \]

We choose normalization so
\[ \langle \Psi_n^0 | \Psi_m^0 \rangle = \delta_{nm} \]
This means that once we find \( \psi_n \) it must be renormalized,

\[
\psi_n \rightarrow \frac{\psi_n}{\langle \psi | \psi_n \rangle}.
\]

Given \( \langle \psi_n | \psi_m \rangle = \delta_{mn} \), \( \langle \psi_n | \psi^n \rangle = 0 \)

we can solve the equation \( \phi = \frac{1}{2} \psi_n \), \( \psi_n \).

We start by considering the case \( n = 1 \)

\[
(H_0 - E_n) \psi_1 = E_1 \psi_1 - V \phi_1.
\]

To find \( E_n \) multiply by \( \langle \psi_n | \psi_1 \rangle \)

\[
\langle \psi_n | (H_0 - E_n) \psi_1 \rangle = E_1 \langle \psi_n | \psi_1 \rangle = - \langle \psi_n | V \phi_1 \rangle.
\]

This gives
\[
E_n' = \langle \psi_n' | V | \psi_n' \rangle
\]
\[
E = E_n + \langle \psi_n' | V | \psi_n' \rangle + \ldots
\]
(to get this we used $\langle \psi_n | \psi_n' \rangle = 1$)

Next multiply both sides by $\langle \psi_m | \psi_n' \rangle$ for $m \neq n$:
\[
(E_n - E_n') \langle \psi_m | \psi_n' \rangle - \langle \psi_m | E_n' | \psi_n' \rangle
\]
\[
= -\langle \psi_m | V | \psi_n' \rangle
\]

This gives
\[
\langle \psi_m | \psi_n' \rangle = -\frac{\langle \psi_m | V | \psi_n' \rangle}{E_n - E_n'}
\]
\[
= \frac{\langle \psi_m | V | \psi_n' \rangle}{E_n - E_n'}
\]

Since
\[
\langle \psi_m | \psi_n' \rangle = 0 \quad n \neq m \quad \text{we get}
\]
\[
| \psi_n' \rangle = \sum_{m=1}^{m_n} \frac{| \psi_m \rangle}{E_n - E_m} \langle \psi_m | V | \psi_n' \rangle
\]
\[
= \sum_{m=1}^{m_n} \frac{| \psi_m \rangle}{E_n - E_m} \langle \psi_m | V | \psi_n' \rangle
\]
Now we know $E_n$ and $\psi_n$. We use this information to calculate $E_n^2$ and $\psi_n^2$.

The starting point is

$$(H_0 - E_n^0) \psi_n^2 = E_n^2 \psi_n^0 = -V\psi_n^1 + 1\psi_n^0 E_n$$

as in the $m=1$ case.

First multiply by $\langle \psi_n^0 | - V\psi_n^1 + 1\psi_n^0 | E_n \rangle = 0 \implies$

$$-E_n^2 = -\langle \psi_n^0 | V \psi_n^0 \rangle + \langle \psi_n^0 | \psi_n^0 \rangle E_n$$

$$E_n^2 = \langle \psi_n^0 | V \psi_n^0 \rangle = \sum_{m \neq n} \frac{\langle \psi_n^0 | V \psi_n^m \rangle \langle \psi_n^m | V \psi_n^0 \rangle}{E_n - E_m}$$

$$= \sum_{m \neq n} \frac{\langle \psi_n^m | V \psi_n^0 \rangle^2}{E_n - E_m}$$
note that if $E_n$ is the ground state the first order correction is negative (consistent with variational method).

We can also compute the second order wave function using $\langle \psi^0_m | m \neq n \rangle$

$$\langle \psi^0_m | (H_0 - E^0_n) | \psi^2_n \rangle = -E \langle \psi^+_n | \psi^0_n \rangle - \langle \psi^0_m | \psi^1_m \rangle + E_n \langle \psi^+_m | \psi^0_n \rangle =$$

$$(E^0_m - E^n_n) \langle \psi^0_m | \psi^2_n \rangle =$$

$$-\sum_{k \neq n} \frac{\langle \psi^0_m | \psi^0_n \rangle \langle \psi^+_n | \psi^1_m \rangle}{(E^0_n - E^0_k)} - \langle \psi^0_n | \psi^1_m \rangle \langle \psi^0_m | \psi^0_n \rangle \frac{1}{E_m - E_n}$$

Dividing by the $(E^0_n - E^0_n)$ give an expression for $\langle \psi^+_m | \psi^2_n \rangle$
\[ \langle \psi_m^0 1 \psi_n^2 \rangle = \frac{1}{(E_n - E_m)} \left\{ \frac{2}{E_n - E_m (E_n - E_r)} \langle \psi_m^0 1 \psi_r^0 \rangle \langle \psi_r^0 1 \psi_n^2 \rangle \right\} \]

This can be used to expand

\[ 1 \psi_n^2 \rangle = \sum_{m \neq n} \langle \psi_m^0 1 \psi_n^2 \rangle \]

while it is possible to continue to any order, normally the first order energy is enough. If \( \langle \psi_n^0 1 \psi_n^0 \rangle = 0 \) then the second order energy should be a good approximation assuming \( V \) is small.
Stark effect - atom in the presence of a weak external electric field

\[ H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} - eEz \]

In this case the first order energy is

\[ E_n = E_n^0 + \langle \psi_n^0 | V | \psi_n^0 \rangle \]

\[ = E_n^0 - eE \langle \psi_n^0 | z | \psi_n^0 \rangle \]

\[ = -\frac{Ze^2}{2\hbar^2} \left( \frac{1}{n+\ell+1} \right)^2 \]

\[ - eE \langle \ell \text{em} | z \psi_0^0 | \ell \text{em} \rangle \]

The first order correction

\[ \psi_{n\ell m}(r) = \frac{1}{r} \psi_m^0 (102) \]
\[ - \frac{Z^2 e^4 m}{2 \hbar^2} \frac{l}{(l+\ell+1)^2} \]

\[ \int_0^\infty u_e(r) u_e(r) \, dr \]

\[ \int v_e^m(x|\theta\phi) \cos \theta v_\ell^0 (\theta\phi) \, d\phi \sin \frac{\pi}{\gamma_1^0 (\theta)} \sqrt{\gamma_3} \]

\[ = - \frac{Z^2 e^4 m}{2 \hbar^2} \frac{l}{(l+\ell+1)^2} + \]

\[ - e \int_0^\infty u_e(r) \, r \, dr \times \sqrt{\gamma_3} \int v_e^m(x|\theta\phi) v_\ell^0 (\theta\phi) v_\ell^m (\theta\phi) \, d\phi \]

The integral over the three spinor harmonic can be performed using properties of \( D_{0m}^\ell (r) \).

Note:

\[ \int d\Omega \, \gamma_e^m (\theta\phi) \gamma_{\ell}^0 (\theta\phi) \gamma_\ell^m (\theta\phi) = \]

\[ \int d\Omega \, \gamma_e^m \cdot C_{\ell m}^{\ell m} \gamma_\ell^m (\theta\phi) = \]

\[ \delta_{\ell \ell} \cdot \delta_{m m} \cdot C_{\ell m}^{\ell m} \]
The shift is

\[- \int_0^\infty \alpha e^{-\lambda} d\lambda = \sqrt{\frac{4\pi}{3}} C_{m,m} E^c \]

If the field is not in the z direction we can use the Wigner-Eckart theorem.