**Quantum Mechanics and Spectroscopy**
**CHEM 3PA3**
**Tutorial 4**

1. Consider the Hamiltonian $\hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{V}$. The first order perturbation for the energy of this system is $\frac{\partial E}{\partial \lambda} = E'(\lambda) = \left\langle \Psi(\lambda) \middle| \hat{V} \middle| \Psi(\lambda) \right\rangle$. If the perturbation parameter can have two possible values, $\lambda_1$, and $\lambda_2$, then $\Psi(\lambda_1)$ yields the lowest energy $E(\lambda_1)$ for $\hat{H}(\lambda_1)$ and $\Psi(\lambda_2)$ yields the lowest energy $E(\lambda_2)$ for $\hat{H}(\lambda_2)$.

   (a) Use the variational principle to show that $\Psi(\lambda_2)$ gives a higher energy for $\hat{H}(\lambda_1)$.

$$\begin{aligned}
E^{trial}_{\Psi(\lambda_2)} &= \left\langle \Psi(\lambda_2) \middle| \hat{H}_{\lambda_1} \middle| \Psi(\lambda_2) \right\rangle \\
&= \left\langle \Psi(\lambda_2) \middle| \hat{H}_0 \middle| \Psi(\lambda_2) \right\rangle + \lambda_1 \left\langle \Psi(\lambda_2) \middle| \hat{V} \middle| \Psi(\lambda_2) \right\rangle \\
E^{ground}_{\Psi(\lambda_1)} &= \left\langle \Psi(\lambda_1) \middle| \hat{H}_0 \middle| \Psi(\lambda_1) \right\rangle + \lambda_1 \left\langle \Psi(\lambda_1) \middle| \hat{V} \middle| \Psi(\lambda_1) \right\rangle \\
E^{trial}_{\Psi(\lambda_2)} &> E^{ground}_{\Psi(\lambda_1)}
\end{aligned}$$

   (b) Repeat this for $\Psi(\lambda_1)$ and $\hat{H}(\lambda_2)$.

$$\begin{aligned}
E^{trial}_{\Psi(\lambda_1)} &= \left\langle \Psi(\lambda_1) \middle| \hat{H}_{\lambda_2} \middle| \Psi(\lambda_1) \right\rangle \\
&= \left\langle \Psi(\lambda_1) \middle| \hat{H}_0 \middle| \Psi(\lambda_1) \right\rangle + \lambda_2 \left\langle \Psi(\lambda_1) \middle| \hat{V} \middle| \Psi(\lambda_1) \right\rangle \\
E^{ground}_{\Psi(\lambda_2)} &= \left\langle \Psi(\lambda_2) \middle| \hat{H}_0 \middle| \Psi(\lambda_2) \right\rangle + \lambda_2 \left\langle \Psi(\lambda_2) \middle| \hat{V} \middle| \Psi(\lambda_2) \right\rangle \\
E^{trial}_{\Psi(\lambda_1)} &> E^{ground}_{\Psi(\lambda_2)}
\end{aligned}$$

   (c) Summing both inequalities, obtain the following expression:

$$E^{trial}_{\Psi(\lambda_2)} + E^{trial}_{\Psi(\lambda_1)} > E^{ground}_{\Psi(\lambda_1)} + E^{ground}_{\Psi(\lambda_2)}$$
$$\lambda_1 \left\langle \Psi(\lambda_2) \middle| \hat{V} \middle| \Psi(\lambda_2) \right\rangle + \lambda_2 \left\langle \Psi(\lambda_1) \middle| \hat{V} \middle| \Psi(\lambda_1) \right\rangle > \lambda_1 \left\langle \Psi(\lambda_1) \middle| \hat{V} \middle| \Psi(\lambda_1) \right\rangle + \lambda_2 \left\langle \Psi(\lambda_2) \middle| \hat{V} \middle| \Psi(\lambda_2) \right\rangle$$
$$\lambda_1 E'(\lambda_2) + \lambda_2 E'(\lambda_1) - \lambda_1 E'(\lambda_1) - \lambda_2 E'(\lambda_2) < 0$$
$$(\lambda_1 - \lambda_2)(E'(\lambda_1) - E'(\lambda_2)) > 0.$$

   (d) Based on this expression, explain what happens to the energy as $\lambda$ increases. If $\lambda_1 > \lambda_2$, then $E'(\lambda_1) < E'(\lambda_2)$, so $E'(\lambda)$ is a decreasing function.

   (e) If $E'(\lambda)$ is differentiable, what would be the behaviour of $E"(\lambda)$? It is negative.

(f) If the perturbation is stabilizing, so that $\left\langle \Psi(\lambda) \middle| \hat{V} \middle| \Psi(\lambda) \right\rangle = E'(\lambda) > 0$, what happens to the slope of the energy as the perturbation becomes stronger. It becomes more negative.

(g) Make an illustrative graph of $E(\lambda)$ vs. $\lambda$.

2. For which of the following systems is the Born-Oppenheimer approximation less justified?

- KBr
- $Si_{60}$
- $UF_6$
- $XeCl_2$

The BO approximation is more important for light atoms. Because F is the lightest, it is less justified for $UF_6$.

3. Why is gravitational attraction between nucleus and electrons neglected in electronic structure calculations?

$$V(r) = -\frac{GM_H m_e}{r}$$
$$V(r) = 1.925185 \times 10^{-57} J$$
$$V(r) = 4.4166 \times 10^{-40}\, Hartree \quad << \quad E_H = -0.5\, Hartree$$

4. A particle of mass $m$ is confined in a one-dimensional box of length $a$. The state of the particle is given by the wavefunction $\Psi(x) = \frac{1}{3}\psi_1(x) + \frac{i}{3}\psi_3(x) - \left(\frac{7}{9}\right)^{1/2}\psi_5(x)$, where $\psi_n(x)$ is a normalized particle-in-a-box wavefunction corresponding to quantum number $n$.

(a) Is the wavefunction $\Psi(x)$ normalized? Yes.

(b) What will be the outcome when the energy of the particle is measured?
$E_1$, $E_3$, or $E_5$, where $E_n = \frac{n^2h^2}{8ma^2}$.

(c) If more than one result is possible, what is the probability of obtaining each result?
$P(E_1) = 1/9$, $P(E_3) = 1/9$, and $P(E_5) = 7/9$.

(d) What is the expectation value of the energy?
$E = E_1P(E_1) + E_3P(E_3) + E_5P(E_5) = \frac{185h^2}{72ma^2}$

(e) Is the wavefunction time-dependent? Yes,

$$\Psi(x,t) = \frac{1}{3}\psi_1(x)e^{-iE_1t/\hbar} + \frac{i}{3}\psi_3(x)e^{-iE_3t/\hbar} - \left(\frac{7}{9}\right)^{1/2}\psi_5(x)e^{-iE_5t/\hbar}$$