Chem. 231B Homework 4 Solutions

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22.11.

1.

\[ \hat{H} = -\frac{1}{2m} \frac{\partial^2}{\partial X^2} - \frac{1}{2} \frac{\partial^2}{\partial x^2} + \frac{1}{2} k(x - X)^2 + \frac{1}{2} K X^2 \]  

(1)

\[ \hat{H} \Psi(x, X) = E \Psi(x, X) \]  

(2)

2.

\[ \hat{H}_e = -\frac{1}{2} \frac{\partial^2}{\partial x^2} + \frac{1}{2} k(x - X)^2 \]  

(3)

\[ \hat{H}_n = -\frac{1}{2} \frac{\partial^2}{\partial X^2} + \frac{1}{2} K X^2 \]  

(4)

With \( \Psi(x, X) = \chi(X) \Psi_e(x) \), Schrödinger’s equation separates into two equations. The first,

\[ \hat{H}_e \Psi_e(x) = E_{el} \Psi_e(x), \]  

(5)

is a harmonic oscillator with \( E_{el} = \omega_e(n_e + \frac{1}{2}) \), where \( \omega_e^2 = k \). The second,

\[ (\hat{H}_n + E_{el}) \chi(X) = E_{tot} \chi(X), \]  

(6)

is also a harmonic oscillator with energy levels \( E_{tot} = \omega_n(n_n + \frac{1}{2}) + E_{el} \), where \( \omega_n = \sqrt{\frac{K}{m}} \).

\[ E_{tot} = \sqrt{k(n_e + \frac{1}{2})} + \sqrt{\frac{K}{m}}(n_n + \frac{1}{2}) \]  

(7)

For \( k = K = 1 \) and \( m = 25 \), \( E_{tot} = (n_e + \frac{1}{2}) + \frac{1}{5}(n_n + \frac{1}{2}) \).

Figure 1 shows the first few energy levels.

3.

The ground state electronic wavefunction is \( \Psi_e = \left( \frac{\sqrt{T}}{\pi} \right)^{1/4} \exp(-\frac{1}{2} \sqrt{k}(x - X)^2) \).

\[ \Delta E = -\frac{1}{2m} \langle \Psi_e \left| \frac{\partial^2}{\partial X^2} \right| \Psi_e \rangle \]  

\[ = \frac{1}{2m} \int_{-\infty}^{\infty} dx \left| \frac{\partial \Psi_e}{\partial X} \right|^2 \]  

\[ = \frac{\pi^{-1/2}}{2m} \int_{-\infty}^{\infty} dx (x - X)^2 e^{-(x - X)^2} \]  

\[ = \frac{\omega_e}{4m} \]  

(8)

For \( k = K = 1 \) and \( m = 25 \), \( \Delta E = \frac{1}{100} \).

4.

Figure 2 shows the different between the exact energy levels and those given by the BO approximation. The greatest deviation is with \( n_n = 0 \). The deviation decreases as \( n_n \) increases.

5.

\[ \omega_{\pm}^2 = \frac{1}{2m} (Mk + K \pm \sqrt{(Mk - K)^2 + 4kK}) \]  

(9)

as \( m \to \infty \), \( M = m + 1 \to m \).
FIG. 2 The first few nuclear and electronic energy levels in the BO approximation (black) compared with the exact result (blue). $E_{tot} = EE[n_e, n_n]$.

\[ \omega^2 \approx \frac{1}{2m} (Mk + K \pm ( Mk - K )) \]  

This gives $\omega_+ = \sqrt{1 + \frac{1}{m} \sqrt{K}} \approx (1 + \frac{1}{2m}) \sqrt{k}$, and $\omega_- = \sqrt{\frac{K}{m}}$. The total energy is

\[ E_{00} \approx \frac{1}{2} \omega_+ + \frac{1}{2} \omega_- = \frac{1}{2} \left( \sqrt{k} + \sqrt{\frac{K}{m}} \right) + \frac{\sqrt{k}}{4m} \]  \tag{11}

The first time is the ground state energy given in the BO approximation and the next term is the leading correction.

6.

Write the Lagrangian equations of motion for the system.

\[ L = \frac{1}{2} \dot{x}^2 + \frac{1}{2} \dot{X}^2 - \frac{1}{2} kx^2 - \frac{1}{2} (k + K)X^2 + kXx \]  \tag{12}

\[ \ddot{x} = -kx + kX \]  \tag{13}

\[ m\ddot{X} = -(k + K)X + kx \]  \tag{14}

In matrix form, this equation becomes

\[ \mathbf{A}\ddot{x} = \mathbf{B}x \]  \tag{15}

where $x = (x, X)$ and

\[ \mathbf{A} = \begin{pmatrix} 1 & 0 \\ 0 & m \end{pmatrix} \]  \tag{16}

\[ \mathbf{B} = \begin{pmatrix} -k & k \\ k & -(k + K) \end{pmatrix} \]  \tag{17}

The equation for a harmonic oscillator always takes the form $\ddot{x} = -\omega^2 x$, so $\omega^2$ will just be the negative of the eigenvalues of $\mathbf{A}^{-1}\mathbf{B}$

\[ \omega^2 = \frac{1}{2m} \left( k + mk + K \pm \sqrt{(k + mk + K)^2 - 4mkK} \right) \]  \tag{18}

Expand inside the square root and simplify

\[ \omega^2 = \frac{1}{2m} \left( Mk + K \pm \sqrt{(Mk - K)^2 + 4kK} \right) \]  \tag{19}

22.12.

1.

FIG. 3 Both $\alpha(R)$ and $\beta(R)$ have the same value at $R = 0$, but $\beta(R)$ approaches 0 as $R \to \infty$ while $\alpha(R)$ approaches $\frac{1}{2}$.

FIG. 4 $K(R)$ has an exponential decay towards 0 while $J(R)$ eventually decays as $\frac{1}{R}$.

FIG. 5 As we expect, $s(R) = 1$ at $R = 0$ (complete overlap) and approaches 0 as $R \to \infty$ (zero overlap).
2.

The total wavefunction is $\Psi = c(\phi_A \pm \phi_B)$, where $c^2 = (2(1 + s))^{-1}$. For the kinetic energy, write $\hat{t} = \hat{h}_A - \hat{v}_A$. For the symmetric (bound) case, let’s expand the expression for $T$

$$T = c^2(\phi_A + \phi_B|\hat{h}_A - \hat{v}_A|\phi_A + \phi_B)$$
$$= c^2\left[\frac{1}{2} - 2(\frac{s}{2}) + \langle \phi_B|\hat{h}_A|\phi_B \rangle - (-1) - 2K - J\right]$$

(20)

To find $\langle \phi_B|\hat{h}_A|\phi_B \rangle$, write

$$H_{BB} = \langle \phi_B|\hat{h}_A + \hat{v}_B|\phi_B \rangle = \langle \phi_B|\hat{h}_A|\phi_B \rangle - 1$$

(21)

Since $H_{BB} = -\frac{1}{2} + J$, then $\langle \phi_B|\hat{h}_A|\phi_B \rangle = \frac{1}{2} + J$. Simplifying the kinetic energy, we get

$$T = \frac{1 - s - 2K}{2(1 + s)}$$

(22)

The potential energy is given by

$$V = c^2(\phi_A + \phi_B|\hat{v}_A + \hat{v}_B|\phi_A + \phi_B)$$
$$= c^2\left[\frac{-1 + 2K + J}{2}\right]$$
$$= \frac{-1 + 2K + J}{1 + s}$$

(23)

The virial theorem predicts that $T = -\frac{1}{2}V$, which is

$$T' = \frac{1 - J - 2K}{2(1 + s)}$$

(24)

Comparing with the actual expression for the kinetic energy, we see that the virial theorem does not hold (unless $J = s$). Figure 7 plots all three expressions as a function of $R$. In the united atom limit, the total ground state energy should be -2 since $Z = 2$ and $E_n = -\frac{Z^2}{2n^2}$. However, $T + V = -1.5$ in this system.

3.

Figures 8, 9 and 10 show the equivalent matrix elements for the $p_z$-orbital (green lines) compared with those of the $s$-orbital (blue lines). $s(R)$ goes negative when the negative and positive lobes overlap and produce a negative contribution to the integral. $K(R)$ switches sign for the same reason. Both $K(R)$ and $J(R)$ has the same united atom limit, which is $-\frac{1}{2}$. As $R \to \infty$, $J(R)$ has a similar $R$ dependence in both cases.

For the $p_x$- or $p_y$-orbital case, the matrix elements will be more similar to the $s$-orbital case. $s(R)$ and $K(R)$ won’t switch sign, but $J(R)$ and $K(R)$ will have the same united atom limit value of $-\frac{1}{2}$. 

FIG. 6 The antibonding energy, $\epsilon_-(R)$, does have a minimum. However, when you add the $\frac{1}{R}$ nuclear repulsion the minimum disappears. Both the bonding and antibonding electronic energies decay as $\frac{1}{R^2}$ at large $R$ (all exponentials go to zero in the expression for $\epsilon_+(R)$). 

FIG. 7 A plot of the kinetic and potential energies of $H_n^z$. $T'(R)$ is the kinetic energy predicted by the virial theorem, which does not match the actual kinetic energy of the system. 

FIG. 8

FIG. 9
If we minimize $\epsilon_+ + \frac{1}{R}$, we get $R_{eq} = 1.24$. For $s \neq 0$, we had $R_{eq} = 2.5$. Thus $s$ is very important.

Choose $J_{eff} = \frac{J}{1+s}$ and $K_{eff} = \frac{K}{1+s}$. This will reproduce the same bonding curve, but will give an inaccurate antibonding curve. If we compare these results with the simple model of the introduction (which interprets the model in terms of only $\alpha$ and $\beta$), we see that we should have $\alpha = -\frac{1}{2} + J_{eff}$ and $\beta = K_{eff}$ so that the simple model reproduces the energy levels

$$\epsilon_{\pm} = \alpha \pm \beta = -\frac{1}{2} + J_{eff} \pm K_{eff}.$$