ChemE 220 - Physical Chemistry II for Engineers – Spring 2025
Solution to Homework Assignment 1

1. Calculate the transition probability between states with quantum numbers *n* and *m*, such that $\Delta n = n - m$. We wish to determine the restrictions on Δn that cause the following integral to be zero or nonzero.

$$\int \psi^*_{\text{final}} \hat{T} \psi_{\text{initial}}\, d\tau \;=\; \int_0^L \left(\frac{2}{L}\right)^{1/2} \sin\frac{n\pi x}{L} [eE_x^0 x] \left(\frac{2}{L}\right)^{1/2} \sin\frac{m\pi x}{L}\, dx \;=\; eE_x^0 \left(\frac{2}{L}\right) \int_0^L x \sin\frac{n\pi x}{L} \sin\frac{m\pi x}{L}\, dx$$

Substitute $\theta = \pi x / L$.

$$\int \psi^* \hat{T} \psi\, d\tau \;=\; eE_x^0 \left(\frac{2L}{\pi^2}\right) \int_0^\pi \theta \sin n\theta \sin m\theta\, d\theta$$

Because we are only concerned if the integral is zero or nonzero, we drop the collection of constants that precedes the integral. Use the trigonometric identity $\sin(n\theta)\sin(m\theta) = \cos((n-m)\theta) - \cos((n+m))\theta$

$$\int \psi^* \hat{T} \psi\, d\tau \;\propto\; \int_0^\pi \theta \big[\cos((n-m)\theta) - \cos((n+m)\theta)\big] d\theta$$

Integrate by parts,

$$\int f\, dg = fg - \int g\, df$$

set $f = \theta$ then $df = d\theta$

set $dg = [\cos(n-m)\theta] d\theta$ then $g = \dfrac{1}{n-m} \sin(n-m)\theta$

$$\int \psi^* \hat{T} \psi\, d\tau \;\propto\; \frac{\theta}{n-m} \sin((n-m)\theta)\bigg|_0^\pi \;-\; \int_0^\pi \frac{\sin((n-m)\theta)}{n-m}\, d\theta \;-\; \frac{\theta}{n+m} \sin((n+m)\theta)\bigg|_0^\pi \;+\; \int_0^\pi \frac{\sin((n+m)\theta)}{n+m}\, d\theta$$

$$\propto\; \frac{\pi}{n-m} \sin((n-m)\pi) \;+\; \frac{\cos((n-m)\theta)}{(n-m)^2}\bigg|_0^\pi \;-\; \frac{\pi}{n+m} \sin((n+m)\pi) \;-\; \frac{\cos((n+m)\theta)}{(n+m)^2}\bigg|_0^\pi$$

Because $n-m$ and $n+m$ are both integers, $\sin((n-m)\pi)$ and $\sin((n+m)\pi)$ are both 0. Evaluate the other terms.

$$\int \psi^* \hat{T} \psi\, d\tau \;\propto\; \frac{1}{(n-m)^2}\big[\cos((n-m)\pi) - 1\big] \;-\; \frac{1}{(n+m)^2}\big[\cos((n+m)\pi) - 1\big]$$

The integral is zero if $\cos((n-m)\pi) = 1$ *and* $\cos((n+m)\pi) = 1$. Therefore, the integral is zero if both $n-m$ and $n+m$ are even integers.

The transition is allowed if $\Delta n = \pm 1, \pm 3, \pm 5, \ldots$

The transition is forbidden if $\Delta n = \pm 2, \pm 4, \pm 6, \ldots$

2. The transition is allowed if

$$\int \psi^*_{\text{final}} \hat{T} \psi_{\text{initial}}\, d\tau \;\neq\; 0$$

In one-dimensional systems, $\hat{T} \;=\; e\, E_x\, x$. Substitute the probability amplitudes and evaluate the integral.

$$\int \psi_1^* \hat{T} \psi_0\, d\tau \;=\; \int_{-\infty}^{\infty} \frac{1}{\sqrt{2}} \left(\frac{b}{\pi}\right)^{1/4} (bx) \mathrm{e}^{-bx^2/2} (eE_x x) \left(\frac{b}{\pi}\right)^{1/4} \mathrm{e}^{-bx^2/2}\, dx \;=\; eE_x b \left(\frac{b}{2\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2 \mathrm{e}^{-bx^2}\, dx$$

Consider the integrand; x^2 and e^{-bx^2} are both positive over the entire range of integration, $-\infty$ to $+\infty$. Thus the integral must be greater than zero.

3. The eigenfunctions of a system are solutions for the Schrödinger equation, $\hat{H}\psi = E\psi$. One can obtain the energies by applying the Hamiltonian to the eigenfunction.

$$\begin{aligned}
\hat{H}\psi &= \left(\frac{-\hbar^2}{2m_e}\frac{\partial^2}{\partial z^2} + \frac{-\hbar^2}{2m_e r^2}\frac{\partial^2}{\partial \phi^2}\right) N \sin\frac{n\pi z}{\ell} e^{im\phi} \\
&= N\frac{-\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial z^2}\sin\frac{n\pi z}{\ell} e^{im\phi} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\sin\frac{n\pi z}{\ell} e^{im\phi}\right) \\
&= \frac{-\hbar^2}{2m_e}\left(\frac{-n^2\pi^2}{\ell^2} + \frac{-m^2}{r^2}\right)\left(N \sin\frac{n\pi z}{\ell} e^{im\phi}\right) \\
&= \frac{\hbar^2}{2m_e}\left(\frac{n^2\pi^2}{\ell^2} + \frac{m^2}{r^2}\right)\psi
\end{aligned}$$

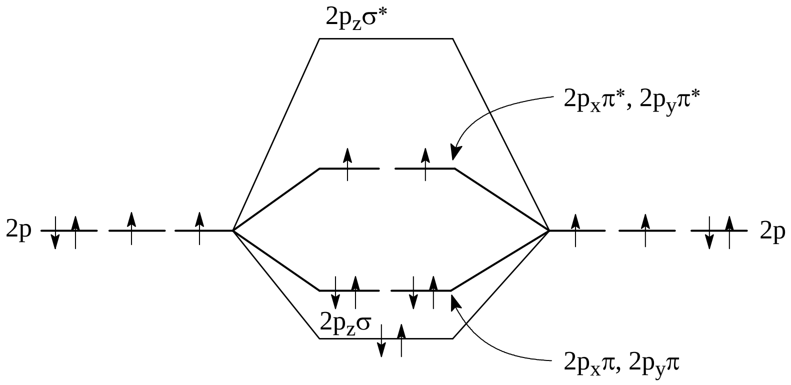
Thus, the energy is the term preceding the eigenfunction,

$$E_{n,m} = \frac{\hbar^2}{2m_e}\left(\frac{n^2\pi^2}{\ell^2} + \frac{m^2}{r^2}\right) \qquad \text{with } n = 1, 2, 3, \ldots \text{ and } m = 0, \pm 1, \pm 2, \ldots$$

4.(A) The dissociation energy is the difference between the lowest vibrational state v = 0 of the molecule and the energy of the separated atoms (at large *R*). Because the vibrational states are not given, use the potential minimum to estimate the energy difference. The potential well for A_2^+ is the deepest - about 6.6 eV. (see the diagram below.)

(B) The force constant is related to the strength of the molecular bond, which is related to the depth and width of the molecular potential curve. The potential curve for A_2^- is the widest and most shallow. A_2^- has the smallest vibrational constant.

(C) To identify the molecule, we need to know the bond order of the diatomic molecule, its positive ion and its negative ion. The molecular orbital energy level diagram for the 2p electrons of O_2 is shown below.

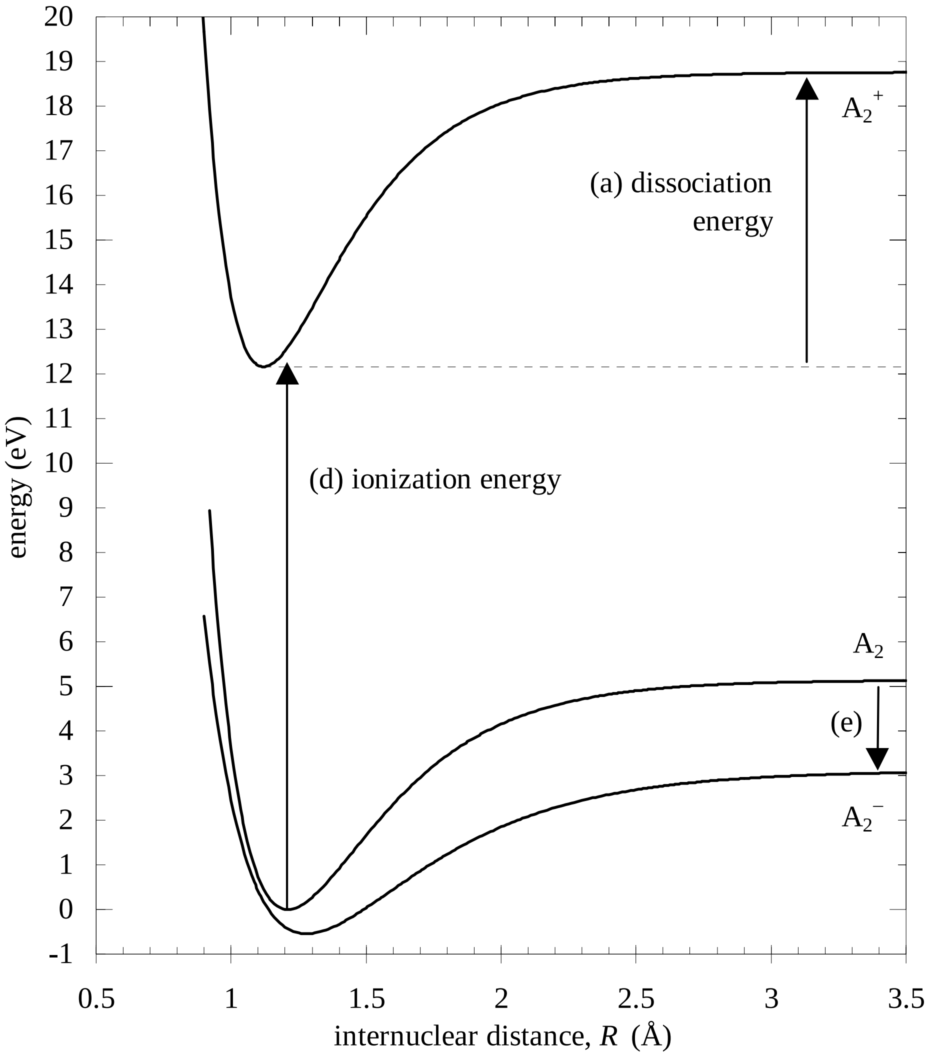


The bond order of O_2 is 2. To form the negative ion, an additional electron goes into a π* antibonding orbital. The bond order of O_2^- is 1½, a weaker bond. To form the positive ion, an electron is extracted from a π* antibonding orbital. The bond order of O_2^+ is 2½, a stronger bond. A similar analysis shows that the bond order of C_2 is 2, the bond order of C_2^- is 2½, and bond order of C_2^+ is 1½. Similarly, the bond order of N_2 is 3, the bond order of N_2^- is 2½, and bond order of N_2^+ is 2½. O_2 is the only molecule of the three whose bond order goes as $A_2^+ > A_2 > A_2^-$. The diatomic is O_2.

(D) This is the difference between the minimum of the A_2 potential and the minimum of the A_2^+ potential, which is 12.5 eV. (see the diagram below.) Because the A_2^+ potential is at higher energy, the reaction $A_2 \rightarrow A_2^+ + e^-$ will require energy, such as the absorption of a UV photon.

(E) Atoms are at large *R* on this diagram. A_2 dissociates to A + A. A_2^- dissociates to A + A^-. The energy difference between A + A and A + A^- is the same as the energy difference between A and A^-. This difference is –2.1 eV, as indicated on the diagram below.

A common error is to measure the distance from the bottom of the potential for A_2 to the bottom of the potential for A_2^-. This distance is the energy of adding an electron to the diatomic, $A_2 + e^- \rightarrow A_2^-$, not the energy of adding an electron to the atom A.



5. The energy of the H 1s orbital is closer to the C 2p than the C 2s. It thus mixes with the C $2p_z$ to form a s bond.

   The C $2p_x$ and $2p_y$ atomic orbitals overlap with the N $2p_x$ and $2p_y$ atomic orbitals. The C $2p_z$ and the N $2p_z$ atomic orbitals also overlap, but less. This is not important because the molecular orbital is unoccupied.