1 Tunneling will bring us together (50 pts)

Applications of the Schrödinger equation to molecules is complicated by the many interactions between electrons and nuclei. Here we'll look at the simplest possible case, H_2.

$$H_A \text{———} H_B$$

1.1 (2 pts) How many of what types of particles make up an H_2 molecule?

2 electrons 1 pt

2 protons 1 pt

1.2 (4 pts) In describing the molecule quantum mechanically, we commonly make the "Born-Oppenheimer," or clamped nucleus, approximation. What is that approximation?

We assume that nuclei are stationary relative to motion of much smaller, faster electrons.

Solve Schrödinger eq for electrons in field of fixed nuclei

1.3 (12 pts) The standard strategy is to describe the molecule in terms of individual electron wavefunctions, often called "orbitals." The equation for the electron wavefunctions of H_2 (in atomic units) is shown below. **Briefly identify the meaning of each term as well as the sign (positive or negative) of the contribution to the H_2 energy.**

$$\left\{-\frac{1}{2}\nabla^2 - \frac{1}{|\mathbf{r}-\mathbf{R}_A|} - \frac{1}{|\mathbf{r}-\mathbf{R}_B|} + \hat{v}_{ee}\right\}\psi_i = \epsilon_i\psi_i$$

1. $-\frac{1}{2}\nabla^2$:

electron Kinetic energy $\langle -\frac{1}{2}\nabla^2 \rangle > 0$

2 2

2. $-\frac{1}{|\mathbf{r}-\mathbf{R}_A|} - \frac{1}{|\mathbf{r}-\mathbf{R}_B|}$:

electron-nucleus attraction $\langle \quad \rangle < 0$

2 2

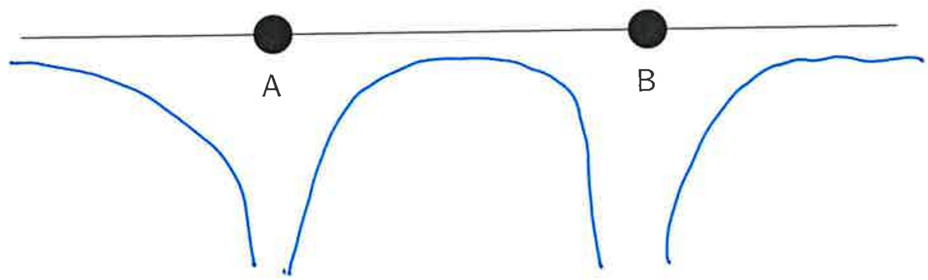
3. $\hat{v}_{ee}$: electron-electron repulsion $\langle \hat{v}_{ee} \rangle > 0$

2 2

1.4 (4 pts) Briefly, why do the electron wavefunctions have to be solved for "self-consistently"?

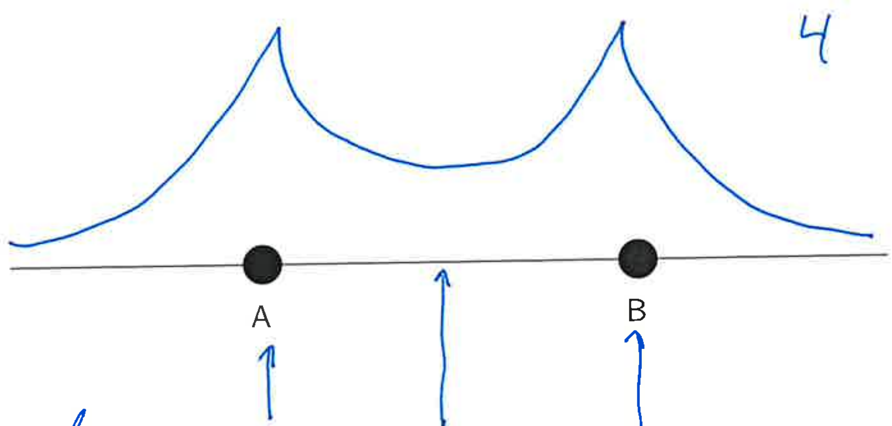
v_{ee} is parametric in all the solutions, $v_{ee}[\psi_i]$. Guess ψ_i, construct v_{ee}, solve for new ψ_i, continue until output = input.

1.5 (4 pts) On the graph below, sketch approximately the potential energy (attraction to the two nuclei A and B) felt by an electron along the axis connecting the two nuclei. (*Hint*: Which term from Equation 1.3 does this correspond to?)



1.6 (8 pts) Let's call the lowest energy solution to the H_2 Schrödinger equation ψ_1. On the graph below, sketch the approximate value of ψ_1 along the internuclear axis. Indicate the location of any nodes, the most probable location(s) of an electron along this axis, and the average location of an electron along this axis. (No calculations required!)

4



no nodes

most probable

average

most probable

1.7 (4 pts) What else, other than the quantities expressed in equation 1.3, contribute to the total internal energy of an H_2 molecule at 0 K? There are two answers; bonus points for identifying both!

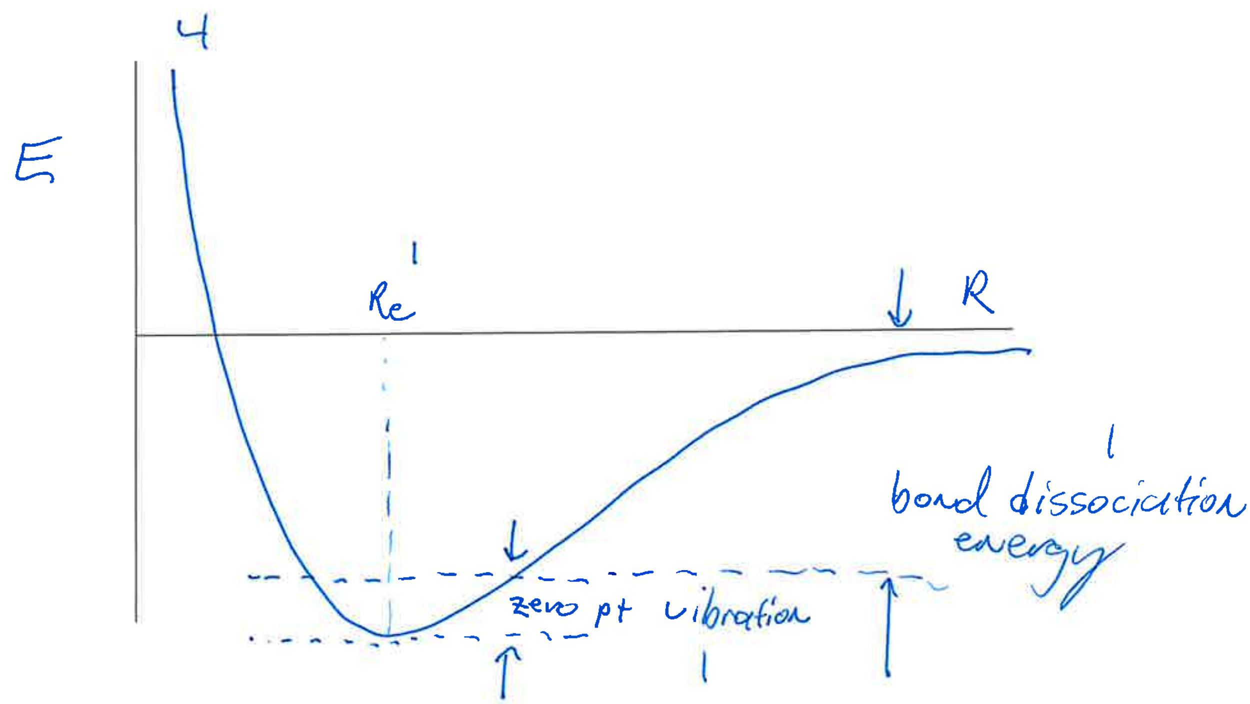
- nucleus - nucleus repulsion energy

$$\frac{e^2}{4\pi\varepsilon_0}\left|\frac{1}{|R_A - R_B|}\right|$$

- nuclear zero point vibrational energy

$$\frac{1}{2}h\nu$$

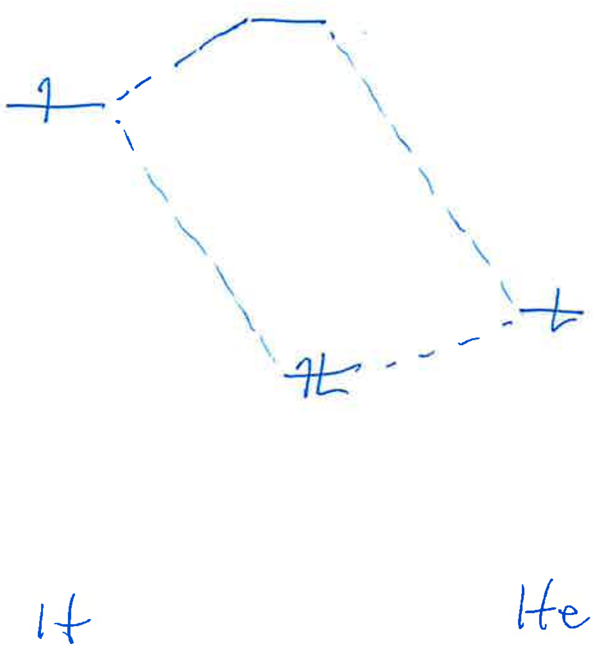
1.8 (8 pts) On the graph below, approximately sketch the H_2 total energy vs interatomic distance. Indicate on the graph the equilibrium internuclear distance (R_e), the bond dissociation energy ($\Delta E(0)$), and the zero point vibrational energy. Remember to properly label both axes, including appropriate units.



1.9 (4 pts) HeH^+ is isoelectronic with H_2 (i.e., same number of electrons and one bonding orbital made up from the H and He 1s orbitals). Do you expect the He—H^+ bond to be stronger or weaker than the H—H one? Why?

weaker 2

poorer energy match between 2
H 1s + He 1s
could say poorer overlap



2 Energy, entropy, temperature (50 pts)

Consider a box that contains $N = 6$ distinguishable marbles, each of which can exist in one of two energy states, 0 or ε.

2.1 (16 pts) Suppose the box is isolated, surrounded by adiabatic walls. Complete the table below for the possible energy states U, their degeneracies Ω, and corresponding entropies of the box (no need to evaluate the logs):

U/ε	Ω	S/k_B
0	1	$\ln 1 = 0$
1	6	ln 6
2	15	ln 15
3	20	ln 20
4	15	ln 15
5	6	ln 6
6	1	ln 1
	12 pts	4 pts

$$\Omega = \binom{6}{n} = \frac{6!}{n!(6-n)!}$$

2.2 (2 pt) What value of U maximizes the entropy of the box?

$$U = 3\epsilon$$

2.3 (8 pts) Imagine this box is put into thermal equilibrium with some large reservoir at temperature T. Write down the partition function $q(\beta)$ for *one marble* in the box, as a function of $\beta = 1/k_B T$.

$$q = \sum_{\epsilon} e^{-\epsilon\beta} = e^{-0\beta} + e^{-\epsilon\beta}$$
$$= 1 + e^{-\epsilon\beta}$$

2.4 (8 pts) Take advantage of the fact that the marbles are identical and ~~in~~distinguishable to write down the partition function $Q(N, \beta)$ of the entire box.

$$Q = q^N = (1 + e^{-\epsilon\beta})^6$$

2.5 (8 pts) Write down an expression for the internal energy of the box as a function of β.

$$U = -N\left(\frac{\partial \ln q}{\partial \beta}\right) = -\cancel{N} \cdot \frac{1}{q}\frac{\partial q}{\partial \beta} \qquad N=6$$

$$= -\frac{N}{q}\left(-\varepsilon e^{-\varepsilon\beta}\right)$$

$$= \frac{N\varepsilon e^{-\varepsilon\beta}}{q}$$

2.6 (4 pts) What is the internal energy of the box in the limit that $\beta \to 0$, ie $T \to \infty$?

$$\lim_{\beta\to 0} q = \lim_{\beta \to 0}\left(1+e^{-\varepsilon\beta}\right) = 2$$

$$\lim_{\beta\to 0} N\varepsilon e^{-\varepsilon\beta} = N\varepsilon$$

$$\lim_{\beta\to 0} U = \frac{N\varepsilon}{2} = \frac{6\varepsilon}{2} = 3\varepsilon$$

2.7 (4 pts) From the results of Question 2.1, what is the entropy of the box in the limit that $\beta \to 0$, ie $T \to \infty$?

$$k_B \ln 20$$

3 Tables