

Chem 30324, Spring 2020, Exam 3

April 14, 2020, 9 am EDT to 9 pm EDT

You have 12 hours to complete this exam. You may refer to the extended outline available on the course website, to the HW 7, HW 8, and HW 9 solutions, and your two pages of written notes, which you must turn in with your solution. When you are done, create a pdf and upload to Gradescope, as you have done with your homeworks.

Your Name:

1. Quantum atoms (15 pts)

Quantum mechanics helps us explain periodic trends in the properties of atoms. Consider the halogens, group 7: F, Cl, Br, I.

1.1 (3 pts) What do you expect for the spin multiplicity of each atom?

$F : 1s^2 2s^2 2p^5$, spin multiplicity: 2, doublets

$Cl : 1s^2 2s^2 2p^6 3s^2 3p^5$, spin multiplicity: 2, doublets

$Br : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$, spin multiplicity: 2, doublets

$I : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$, spin multiplicity: 2, doublets

1.2 (3 pts) Rank the atoms in terms of their first ionization energy (i.e., minimum energy to remove a valence electron).

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In [5]: print('I<Br<Cl<F')
```

I<Br<Cl<F

1.3 (3 pts) Rank the atoms in terms of the frequency of light ($h\nu$) necessary to eject a 1s electron from them.

```
In [6]: print('F<Cl<Br<I')
```

```
F<Cl<Br<I
```

1.4 (3 pts) All the halogens exist as dimers in their elemental state (F_2 , Cl_2 , ...). Rank the dimeric elements according to increasing boiling point.

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In [7]: print('Boiling point: F2<Cl2<Br2<I2')
```

```
Boiling point: F2<Cl2<Br2<I2
```

1.5 (3 pts) The halogen dimers all have a bond order of 1. Do they all have the same bond energy? If not, which do you think will have the strongest bond?

```
In [2]: print('No. They have different bond energies. I (WFS) would have guessed  
F-F would have strongest bond. In fact, it is the weakest. The other thr  
ee have similar energies.')
```

```
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```

Dimer	Bond energy
F2	158 kJ/mol
Cl2	242
Br2	224
I2	214

2. Tunneling will bring us together (53 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 .

2.1 (2 pts) How many of what types of particles make up an H_2 molecule?

```
In [3]: print('Two nuclei and two electrons make up an H2 molecule')
```

```
Two nuclei and two electrons make up an H2 molecule
```

2.2 (4 pts) In describing the molecule quantum mechanically, we commonly make the "Born-Oppenheimer" approximation? What is that approximation?

```
In [4]: print('Born–Oppenheimer (BO) approximation is the assumption that the motion of atomic nuclei and electrons in a molecule can be decoupled. We treat the nuclei as "clamped" in space and solve the Schrodinger equation for the electrons.')
```

Born–Oppenheimer (BO) approximation is the assumption that the motion of atomic nuclei and electrons in a molecule can be decoupled. We treat the nuclei as "clamped" in space and solve the Schrodinger equation for the electrons.

2.3 The standard strategy is to describe the molecule in terms of individual electron wavefunctions, often called "orbitals." The equation for the electron wavefunctions of H₂ (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 H₂ energy.**

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

2.3.1 (3 pts)

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

```
In [4]: print('Kinetic energy. Always positive.')
```

Kinetic energy. Always positive.

2.3.2 (3 pts)

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

```
In [5]: print('Attraction between the electron and two nuclei. Negative.')
```

Attraction between the electron and two nuclei. Negative.

2.3.3 (3 pts)

$$\hat{v}_{\text{Coulomb}}$$

```
In [6]: print('Classical repulsion between distinguishable electron "clouds". Positive.')
```

Classical repulsion between distinguishable electron "clouds". Positive.

2.3.4 (3 pts)

$$\hat{v}_{\text{exchange}}$$

```
In [6]: print('Accounts for electron indistinguishability (Pauli principle for fermions).')
print('Decreases Coulomb repulsion because electrons of like spin intrinsically avoid one another. Negative')
```

Accounts for electron indistinguishability (Pauli principle for fermions).

Decreases Coulomb repulsion because electrons of like spin intrinsically avoid one another. Negative

2.3.4 (3 pts)

$$\hat{v}_{\text{correlation}}$$

```
In [8]: print('Decrease in Coulomb repulsion due to dynamic ability of electrons to avoid one another; "fixes" orbital approximation. Negative.')
```

Decrease in Coulomb repulsion due to dynamic ability of electrons to avoid one another; "fixes" orbital approximation. Negative.

2.4 (4 pts) Briefly, why do the electron wavefunctions have to be solved for "self-consistently"?

The potential energy terms of the Schrodinger eq are functions ("functionals") of the wavefunctions themselves. Therefore, the only way to solve is to guess wavefunctions, solve for new ones, update your guess, and repeat until input and output wavefunctions are the same!

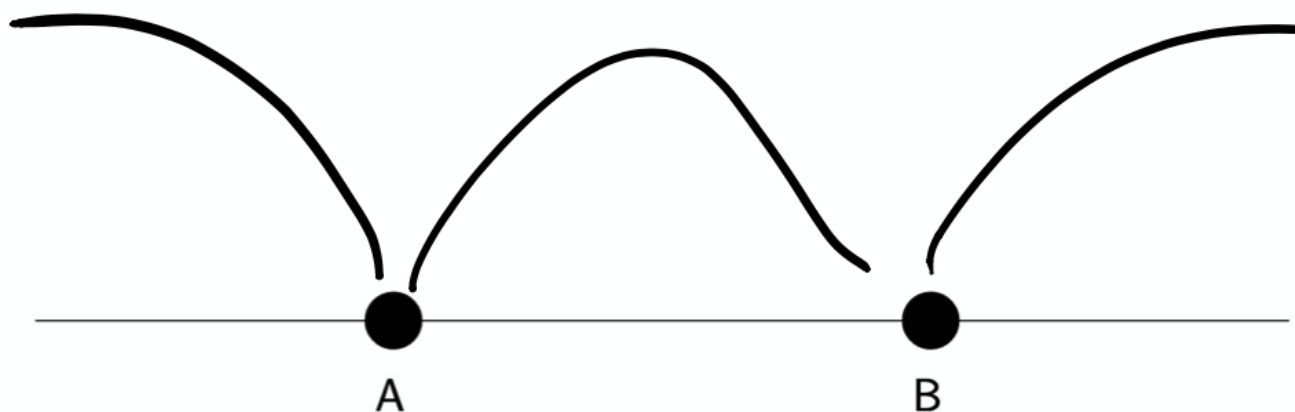
2.5 (4 pts) Briefly, how might the *variational principle* be helpful in solving the Schrödinger equation?

The variational principle guarantees that the expectation value of the energy of a guessed wavefunction is always greater than that of the true lowest energy solution.

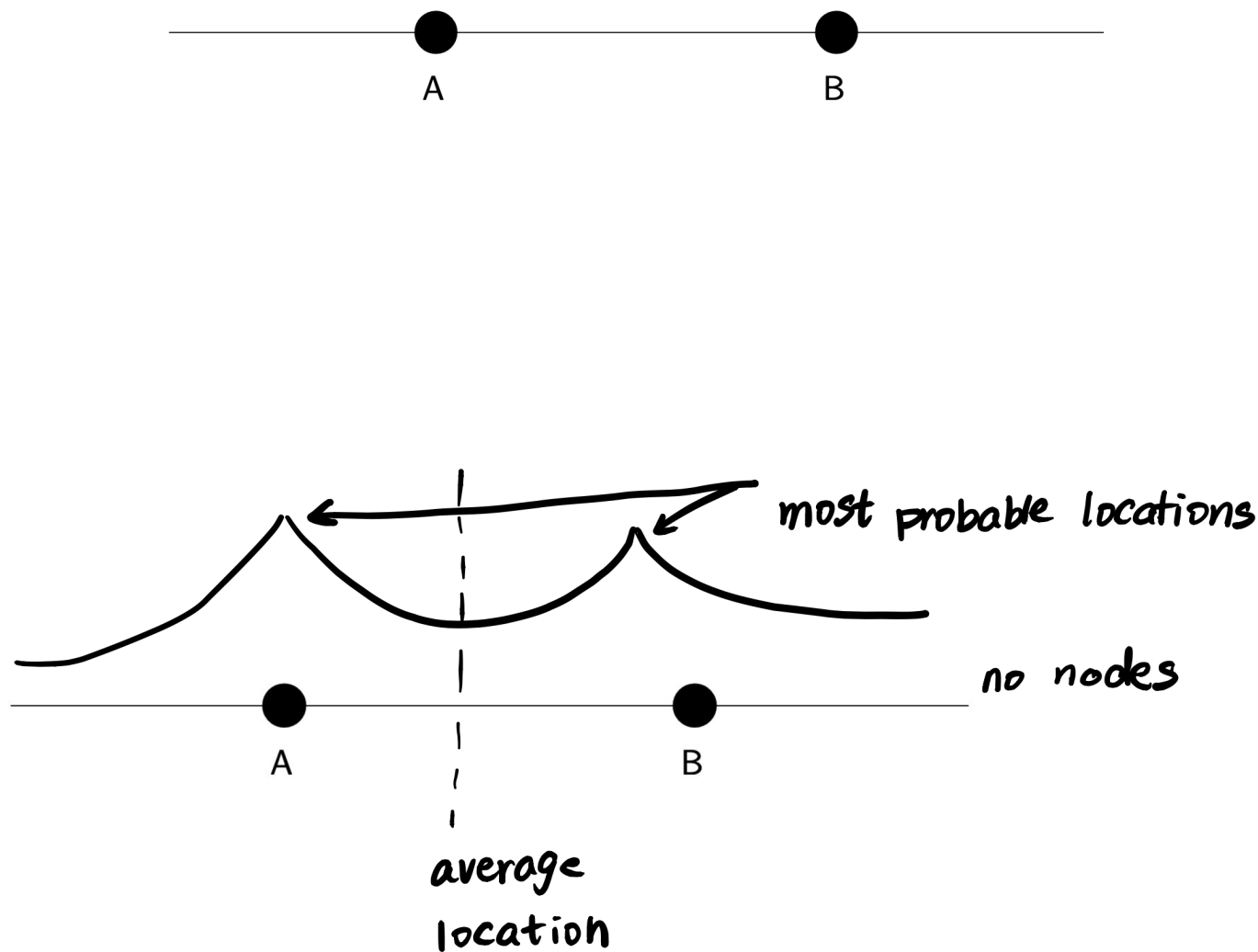
$$\langle \psi_{\text{trial}}^{\lambda} | \hat{H} | \psi_{\text{trial}}^{\lambda} \rangle = E_{\text{trial}}^{\lambda} \geq E_0$$

It allows us to judge the relative qualities of guesses; lowest energy guess is closest to the truth!

2.6 (4 pts) On the graph below, approximately sketch 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 2.3 does this correspond to?)



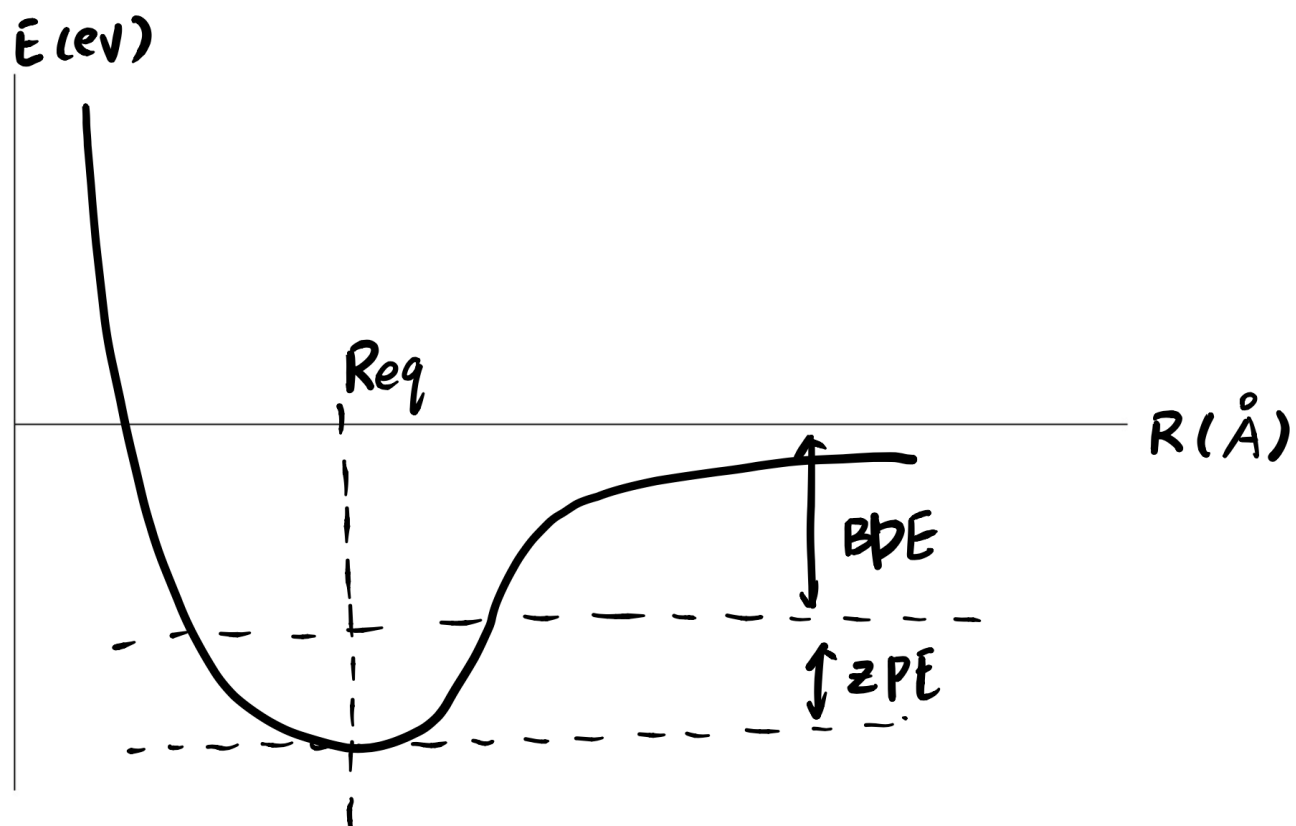
2.7 (8 pts) Let's call the lowest energy solution to the H_2 Schrödinger equation ψ_1 . On the graph below, sketch the approximate value of ψ_1 along the internuclear axis. Indicate the location of any nodes, the most probable location(s) of an electron along this axis, and the average location of an electron along this axis. (No calculations required!)



2.8 (4 pts) What else, other than the quantities expressed in equation 2.3, contribute to the total internal energy of an H_2 molecule at 0 K? There are two answers; bonus points for identifying both!

- 1) Electrostatic repulsion between the two nuclei, $1/|R_A - R_B|$
- 2) Zero-point vibrational kinetic energy of the nuclei

2.9 (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.



3. Energy, entropy, temperature (32 pts)

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

3.1 (7 pts) Suppose the box is isolated, surrounded by adiabatic walls. Complete the table below for the possible internal energy states U , their degeneracies, and corresponding entropies of the box:

U/ϵ	Ω	S/k_B
0	1	$\ln 1 = 0$
1	6	$\ln 6 = 1.79$
2	15	$\ln 15 = 2.71$
3	20	$\ln 20 = 3.00$
4	15	$\ln 15 = 2.71$
5	6	$\ln 6 = 1.79$
6	1	$\ln 1 = 0$

3.2 (1 pt) What value of U maximizes the entropy of the box?

The entropy of the box reaches the maximum at U equals to 3ϵ .

3.3 (8 pts) Imagine this box is put into thermal equilibrium with some big reservoir of temperature T . Write down the partition function $Q(N, T)$ for the box as a function of $\beta = 1/k_B T$.

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

3.4 (8 pts) Write down an expression for the internal energy U of the box as a function of $\beta = 1/k_B T$.

$$\langle U \rangle = - \left(\frac{d \ln Q}{d\beta} \right) = - \frac{N}{q} \left(\frac{dq}{d\beta} \right) = - \frac{N}{q} \frac{d(1 + e^{-\beta\epsilon})}{d\beta} = \frac{N\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}},$$

3.5 (4 pts) What is the internal energy of the box in the limit that $\beta \rightarrow 0$, ie $T \rightarrow \infty$?

$$\langle U \rangle = \frac{N\epsilon}{2} = 3\epsilon \text{ in the limit that } \beta \rightarrow 0$$

3.6 (4 pts) From the results of question 3.1, what is the entropy of the box in the limit that $\beta \rightarrow 0$, ie $T \rightarrow \infty$?

The entropy is $k_B \ln 20 = 3k_B$ in the limit that $\beta \rightarrow 0$. Maximum T maximizes entropy.

In []: