Quiz 1

Chemistry 3BB3; Winter 2003

Name/PID:

1. **The Born-Oppenheimer approximation is used to separate the electronic and nuclear motions in a molecule. This approximation is accurate because.**
   (a) The atomic nuclei in a molecule do not move.
   (b) The nuclei in a molecule move much more slowly than the electrons in the molecule.
   (c) The nuclei and electrons in a molecule move at almost exactly the same speed.
   (d) The electrons in a molecule move much more slowly than the atomic nuclei.
   (e) The electrons in a molecule do not move.
   (f) None of the above.

2. **The Schrödinger equation for a 2-electron, 2-atom molecule is written below, in atomic units. Cross out the terms that are ignored in the Born-Oppenheimer approximation.**

$$
\begin{aligned}
&\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)\left(-\tfrac{\nabla^2_{\boldsymbol{R}_1}}{2M_1}-\tfrac{\nabla^2_{\boldsymbol{R}_2}}{2M_2}\right)\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)+\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\left(-\tfrac{\nabla^2_{\boldsymbol{R}_1}}{2M_1}-\tfrac{\nabla^2_{\boldsymbol{R}_2}}{2M_2}\right)\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)\\
&-\frac{\nabla_{\boldsymbol{R}_1}\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\cdot\nabla_{\boldsymbol{R}_1}\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)}{M_1}-\frac{\nabla_{\boldsymbol{R}_2}\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\cdot\nabla_{\boldsymbol{R}_2}\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)}{M_2}\\
&+\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\left(-\tfrac{\nabla^2_{\boldsymbol{r}_1}}{2}-\tfrac{\nabla^2_{\boldsymbol{r}_2}}{2}+\tfrac{Z_1Z_2}{|\boldsymbol{R}_1-\boldsymbol{R}_2|}-\tfrac{Z_1}{|\boldsymbol{r}_1-\boldsymbol{R}_1|}-\tfrac{Z_2}{|\boldsymbol{r}_1-\boldsymbol{R}_2|}-\tfrac{Z_1}{|\boldsymbol{r}_2-\boldsymbol{R}_1|}-\tfrac{Z_2}{|\boldsymbol{r}_2-\boldsymbol{R}_2|}+\tfrac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\right)\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)\\
&=E\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)
\end{aligned}
$$

Use the following definitions in problems 3 and 4.

$$
\begin{aligned}
\hat{T}_e &\equiv -\tfrac{\nabla^2_{\boldsymbol{r}_1}}{2}-\tfrac{\nabla^2_{\boldsymbol{r}_2}}{2}\\
\hat{V}_{ne} &\equiv -\tfrac{Z_1}{|\boldsymbol{r}_1-\boldsymbol{R}_1|}-\tfrac{Z_2}{|\boldsymbol{r}_1-\boldsymbol{R}_2|}-\tfrac{Z_1}{|\boldsymbol{r}_2-\boldsymbol{R}_1|}-\tfrac{Z_2}{|\boldsymbol{r}_2-\boldsymbol{R}_2|}\\
\hat{V}_{ee} &\equiv \tfrac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\\
\hat{V}_{nn} &\equiv \tfrac{Z_1Z_2}{|\boldsymbol{R}_1-\boldsymbol{R}_2|}\\
\hat{T}_n &\equiv -\tfrac{\nabla^2_{\boldsymbol{R}_1}}{2M_1}-\tfrac{\nabla^2_{\boldsymbol{R}_2}}{2M_2}
\end{aligned}
$$

3. **Using the preceding notation and your result from problem 2, write the Schrödinger equation for the electrons in the Born-Oppenheimer Approximation.**

4. **Using the preceding notation and your results from problems 2 and 3, write the Schrödinger equation for the nuclei in the Born-Oppenheimer Approximation.**

(FLIP OVER for Problems 5-10)

We discussed atomic units, where the mass of the electron, the charge of the electron, $\hbar$, etc. are assumed to be zero. These questions test your knowledge of atomic units.

5. **The atomic unit of energy is the:**
   (a) Bohr.
   (b) Schrödinger.
   (c) Slater.
   (d) Oppenheimer.
   (e) None of the above.

6. **The atomic unit of length is the**
   (a) Bohr.
   (b) Schrödinger.
   (c) Slater.
   (d) Oppenheimer.
   (e) None of the above.

7. **The activation energy in many chemical reactions is about 15-25 $^{kcal}\!/\!_{mol}$. This is**
   (a) much smaller than the atomic unit of energy.
   (b) much larger than the atomic unit of energy.
   (c) about the same size as the atomic unit of energy.

8. **Infrared spectroscopic measurements of vibrational transitions in molecules are resolved to about 1 cm^{-1}. This is**
   (a) much smaller than the atomic unit of energy.
   (b) much larger than the atomic unit of energy.
   (c) about the same size as the atomic unit of energy.

9. **The radius of a proton is about $10^{-15}\ m$. This is**
   (a) much smaller than the atomic unit of length.
   (b) much larger than the atomic unit of length.
   (c) about the same size as the atomic unit of length.

10. **The distance of an electron orbiting the nucleus in the "old" semiclassical quantum theory derived by Bohr (long before the Schrödinger equation!) is $.52 \cdot 10^{-10}\ m$. This is**
   (a) much smaller than the atomic unit of length.
   (b) much larger than the atomic unit of length.
   (c) about the same size as the atomic unit of length.

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1. **The Born-Oppenheimer approximation is used to separate the electronic and nuclear motions in a molecule. This approximation is accurate because.**
   (a) The atomic nuclei in a molecule do not move.
   (b) The nuclei in a molecule move much more slowly than the electrons in the molecule.
   (c) The nuclei and electrons in a molecule move at almost exactly the same speed.
   (d) The electrons in a molecule move much more slowly than the atomic nuclei.
   (e) The electrons in a molecule do not move.
   (f) None of the above.

2. **The Schrödinger equation for a 2-electron, 2-atom molecule is written below, in atomic units. Cross out the terms that are ignored in the Born-Oppenheimer approximation.**

$$
\begin{aligned}
&\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)\left(-\tfrac{\nabla^2_{\boldsymbol{R}_1}}{2M_1}-\tfrac{\nabla^2_{\boldsymbol{R}_2}}{2M_2}\right)\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)+\cancel{\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\left(-\tfrac{\nabla^2_{\boldsymbol{R}_1}}{2M_1}-\tfrac{\nabla^2_{\boldsymbol{R}_2}}{2M_2}\right)\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)}\\
&\cancel{-\frac{\nabla_{\boldsymbol{R}_1}\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\cdot\nabla_{\boldsymbol{R}_1}\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)}{M_1}-\frac{\nabla_{\boldsymbol{R}_2}\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\cdot\nabla_{\boldsymbol{R}_2}\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)}{M_2}}\\
&+\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\left(-\tfrac{\nabla^2_{\boldsymbol{r}_1}}{2}-\tfrac{\nabla^2_{\boldsymbol{r}_2}}{2}+\tfrac{Z_1Z_2}{|\boldsymbol{R}_1-\boldsymbol{R}_2|}-\tfrac{Z_1}{|\boldsymbol{r}_1-\boldsymbol{R}_1|}-\tfrac{Z_2}{|\boldsymbol{r}_1-\boldsymbol{R}_2|}-\tfrac{Z_1}{|\boldsymbol{r}_2-\boldsymbol{R}_1|}-\tfrac{Z_2}{|\boldsymbol{r}_2-\boldsymbol{R}_2|}+\tfrac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\right)\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)\\
&=E\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)
\end{aligned}
$$

Use the following definitions in problems 3 and 4.

$$\hat{T}_e \equiv -\tfrac{\nabla^2_{\boldsymbol{r}_1}}{2}-\tfrac{\nabla^2_{\boldsymbol{r}_2}}{2}$$

$$\hat{V}_{ne} \equiv -\tfrac{Z_1}{|\boldsymbol{r}_1-\boldsymbol{R}_1|}-\tfrac{Z_2}{|\boldsymbol{r}_1-\boldsymbol{R}_2|}-\tfrac{Z_1}{|\boldsymbol{r}_2-\boldsymbol{R}_1|}-\tfrac{Z_2}{|\boldsymbol{r}_2-\boldsymbol{R}_2|}$$

$$\hat{V}_{ee} \equiv \tfrac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}$$

$$\hat{V}_{nn} \equiv \tfrac{Z_1Z_2}{|\boldsymbol{R}_1-\boldsymbol{R}_2|}$$

$$\hat{T}_n \equiv -\tfrac{\nabla^2_{\boldsymbol{R}_1}}{2M_1}-\tfrac{\nabla^2_{\boldsymbol{R}_2}}{2M_2}$$

3. **Using your result from problem 2, write the Schrödinger equation for the electrons in the Born-Oppenheimer Approximation.**

$$\left(\hat{T}_e+\hat{V}_{nn}+\hat{V}_{ne}+\hat{V}_{ee}\right)\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)=E\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)$$

4. **Using your results from problems 2 and 3, write the Schrödinger equation for the nuclei in the Born-Oppenheimer Approximation.**

$$\left(\hat{T}_n+E\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\right)\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)=E^{BO}_{total}\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)$$

(FLIP OVER for Problems 5-10)

We discussed atomic units, where the mass of the electron, the charge of the electron, $\hbar$, etc. are assumed to be zero.

5. **The atomic unit of energy is the:**
   (a) Bohr.
   (b) Schrödinger.
   (c) Slater.
   (d) Oppenheimer.
   (e) None of the above. The atomic unit of energy is the Hartree.

6. **The atomic unit of length is the**
   (a) Bohr.
   (b) Schrödinger.
   (c) Slater.
   (d) Oppenheimer.
   (e) None of the above.

7. **The activation energy in many chemical reactions is about 15-25 $kcal/mol$. This is**
   (a) much smaller than the atomic unit of energy. There are about 630 $kcal/mol$ in one Hartree
   (b) much larger than the atomic unit of energy.
   (c) about the same size as the atomic unit of energy.

8. **Infrared spectroscopic measurements of vibrational transitions in molecules are resolved to about 1 cm^{-1}. This is**
   (a) much smaller than the atomic unit of energy. There are about 22000 cm^{-1} in one Hartree.
   (b) much larger than the atomic unit of energy.
   (c) about the same size as the atomic unit of energy.

9. **The radius of a proton is about $10^{-15}\ m$. This is**
   (a) much smaller than the atomic unit of length. A Bohr is about $5 \cdot 10^{-11}\ m$.
   (b) much larger than the atomic unit of length.
   (c) about the same size as the atomic unit of length.

10. **The distance of an electron orbiting the nucleus in the "old" semiclassical quantum theory derived by Bohr (long before the Schrödinger equation!) is $.52 \cdot 10^{-10}\ m$. This is**
    (a) much smaller than the atomic unit of length.
    (b) much larger than the atomic unit of length.
    (c) about the same size as the atomic unit of length. This is why the atomic unit of length is called the Bohr!