Name________________________________ Student #____________________________

Quiz 7
CHEM 3PA3; Fall 2018

This quiz has 8 problems worth 12 points each. The first four problems go together and the last three problems go together.

1-2. Write the electronic and nuclear Hamiltonians for the Hydrogen molecule within the Born-Oppenheimer approximation. Do not use atomic units. (That is, write out the dependence on fundamental constants.)

3. In one dimension, the Heisenberg Uncertainty Principle for position and momentum states that $\left(\langle x^2\rangle - \langle x\rangle^2\right)\left(\langle \hat{p}^2\rangle - \langle \hat{p}\rangle^2\right) \geq \tfrac{1}{2}\left[x,\hat{p}\right]$**. What is the value of** $\left[x,\hat{p}\right]$**?**

4. For a light (nonrelativisitic) atom or molecule in the absence of a magnetic field, the squared-magnitude total spin of an electron and its total electronic energy can be observed simultaneously. This means that (circle all that apply)

(a) the operators $\hat{S}^2$ and $\hat{H}$ commute.

(b) the operators $\hat{S}^2$ and $\hat{H}$ do not commute.

(c) $\hat{S}^2\hat{H} - \hat{H}\hat{S}^2 = 0$.

(d) $\hat{S}^2\hat{H} + \hat{H}\hat{S}^2 = 0$.

(e) The eigenfunctions of $\hat{H}$ can also be chosen to be eigenfunctions of $\hat{S}^2$.

(f) The eigenvalues of $\hat{H}$ can also be chosen to be eigenvalues of $\hat{S}^2$.

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5,6. **Fill in the eigenvalues for the total angular momentum squared, $\hat{J}^2$, and the total angular momentum around the *z*-axis for a spherical Harmonic.**

$$\hat{J}^2 Y_J^{M_J} = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ Y_J^{M_J}$$

$$\hat{J}_z Y_J^{M_J} = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ Y_J^{M_J}$$

7-8. **Convert the following expressions from integral notation into bra-ket notation.**

$$\int \left(\hat{A} \Psi(x) \right)^* \Phi(x) \, dx =$$

$$\iint \Phi^*(\mathbf{r}_1, \mathbf{r}_2) \left(\tfrac{-1}{2} \nabla_1^2 - \tfrac{1}{2} \nabla_2^2 \right) \Psi(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2$$

Bonus: (5 points) Sketch the effective nuclear charge felt by an electron *r* units from the nucleus for the Beryllium dication, Be^{2+}. Clearly specify the appropriate limits as $r \to 0$ and $r \to +\infty$.

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1-2. Write the electronic and nuclear Hamiltonians for the Hydrogen molecule within the Born-Oppenheimer approximation. Do not use atomic units. (That is, write out the dependence on fundamental constants.)

electronic Schrodinger Eq.

$$\begin{pmatrix} -\frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_1} - -\frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_2} + \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1-\mathbf{r}_2|} + \frac{e^2}{4\pi\varepsilon_0|\mathbf{R}_1-\mathbf{R}_2|} \\ -\frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1-\mathbf{R}_1|} - \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1-\mathbf{R}_2|} - \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_2-\mathbf{R}_1|} - \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_2-\mathbf{R}_2|} \end{pmatrix} \psi_{el}\left(\mathbf{r}_1,\mathbf{r}_2|\mathbf{R}_1,\mathbf{R}_2\right) = U\left(\mathbf{R}_1,\mathbf{R}_2\right)\psi_{el}\left(\mathbf{r}_1,\mathbf{r}_2|\mathbf{R}_1,\mathbf{R}_2\right)$$

nuclear Schrodinger Eq.

$$\left(-\frac{\hbar^2}{2M_H}\nabla^2_{\mathbf{R}_1} - \frac{\hbar^2}{2M_H}\nabla^2_{\mathbf{R}_2} + U\left(\mathbf{R}_1,\mathbf{R}_2\right)\right)\chi_{nuc}\left(\mathbf{R}_1,\mathbf{R}_2\right) = E_{\text{total}}\chi_{nuc}\left(\mathbf{R}_1,\mathbf{R}_2\right)$$

3. In one dimension, the Heisenberg Uncertainty Principle for position and momentum states that $\left(\langle x^2\rangle - \langle x\rangle^2\right)\left(\langle \hat{p}^2\rangle - \langle \hat{p}\rangle^2\right) \geq \frac{1}{2}[x,\hat{p}]$. What is the value of $[x,\hat{p}]$?

Using the fact the momentum operator in one dimension is $-i\hbar\frac{d}{dx}$ we need to evaluate the action of the commutator on an arbitrary wavefunction, $\Psi(x)$.

$$\begin{aligned}[x,\hat{p}]\Psi(x) &= \left[x,-i\hbar\tfrac{d}{dx}\right]\Psi = \left(x\left(-i\hbar\tfrac{d}{dx}\right) - \left(-i\hbar\tfrac{d}{dx}\right)x\right)\Psi(x) \\ &= -i\hbar\left(x\tfrac{d\Psi}{dx} - \tfrac{d(x\Psi(x))}{dx}\right) = -i\hbar\left(x\tfrac{d\Psi}{dx} - x\tfrac{d\Psi}{dx} - \Psi(x)\tfrac{dx}{dx}\right) = i\hbar\Psi(x)\cdot(1) \\ &= i\hbar\Psi(x)\end{aligned}$$

therefore

$$[x,\hat{p}] = i\hbar$$

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5,6. Fill in the eigenvalues for the total angular momentum squared, $\hat{J}^2$, and the total angular momentum around the *z*-axis for a spherical Harmonic.

$$\hat{J}^2 Y_J^{M_J} = \underline{\hbar^2 J(J+1)} Y_J^{M_J}$$

$$\hat{J}_z Y_J^{M_J} = \underline{\hbar M_J} Y_J^{M_J}$$

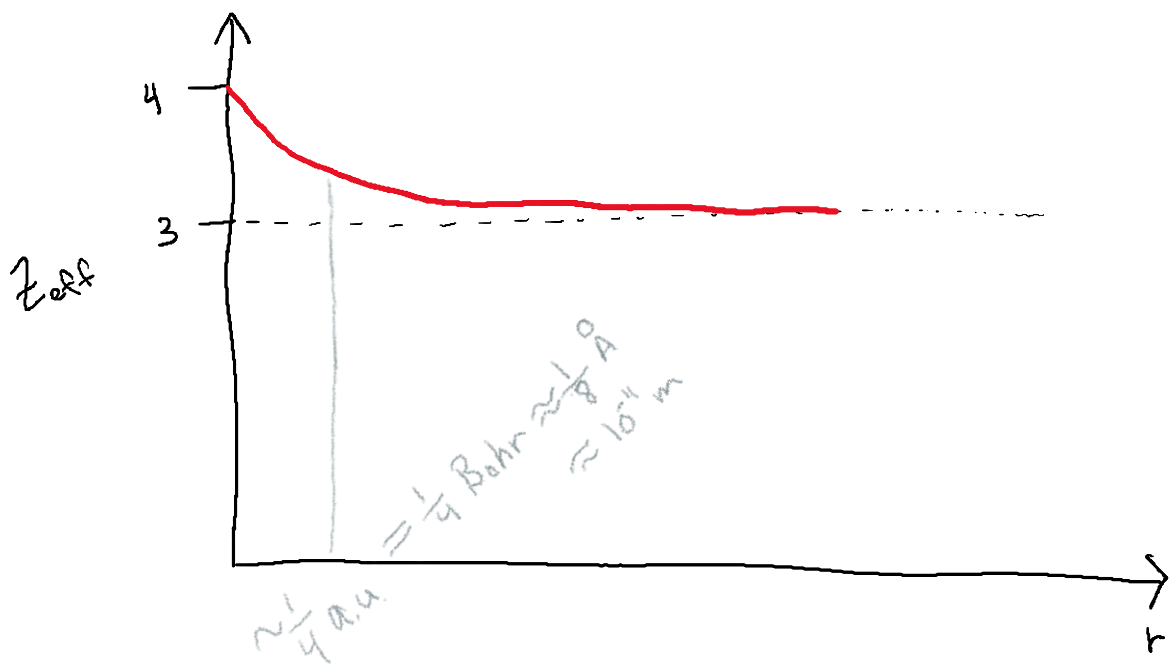
7-8. Convert the following expressions from integral notation into bra-ket notation.

$$\int \left(\hat{A}\Psi(x)\right)^* \Phi(x)\,dx = \langle A\Psi | \Phi \rangle$$

$$\iint \Phi^*(\mathbf{r}_1,\mathbf{r}_2)\left(\tfrac{-1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2\right)\Psi(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2 = \left\langle \Phi \left| \tfrac{-1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 \right| \Psi \right\rangle$$

Bonus: (5 points) Sketch the effective nuclear charge felt by an electron *r* units from the nucleus for the Beryllium dication, Be^{2+}. Clearly specify the appropriate limits as $r \to 0$ and $r \to +\infty$.

This is a 2-electron atom. Near the nucleus, an electron feels the entire nuclear charge (+4). Far from the nucleus, the electron "sees" the nucleus (+4 charge) and the other electron (which is closer to the nucleus almost certainly (-1 charge) for a total charge of +3. The other electron can be assumed to be in 1*s*-like orbital (the electron that is far away makes the electron that is close to the nucleus feel like it is in a 1-electron atom) so the effective nuclear charge decays relatively quickly, on a length scale similar to the radius of the *s*-type orbital (which is about ¼ the size it was in a hydrogen atom). So a rough sketch would be:



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