Name__________________________________ Student #___________________________

Quiz 5
CHEM 3PA3; Fall 2018

This quiz has 5 problems worth 20 points each.

1. Write the molecular Hamiltonian for a N-electron P-atom molecule. Show the dependence on fundamental constants. (I.e., do not use atomic units.)

2,3. Write the electronic Schrödinger equation and the nuclear Schrödinger equation for a N-electron P-atom molecule. You may use atomic units.

Electronic Schrödinger Equation:

Nuclear Schrödinger Equation:

4. Describe the Born-Oppenheimer approximation *in words*, taking care to make it clear what the fundamental approximation is.

5. The energy eigenvalues of a 1-electron atom become ______ as the principle quantum number, *n*, increases.

(a) closer together (b) further apart

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Bonus: (10 points) What is the normalization constant for the ground state of the hydrogenic atom in atomic units. Remember that in spherical coordinates, an integral of a function over all space has the form

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} f\left(r,\theta,\phi\right) r^2 \sin\theta d\phi d\theta dr .$$

The following integral may be useful,

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \qquad\qquad n = 1, 2, \ldots$$

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1. Write the molecular Hamiltonian for a N-electron P-atom molecule. Show the dependence on fundamental constants. (I.e., do not use atomic units.)

$$\hat{H}_{\text{molecule}} = \underbrace{\sum_{A=1}^{P} -\frac{\hbar^2}{2m_A}\nabla_A^2}_{\substack{\text{nuclear}\\ \text{kinetic energy}}} + \underbrace{\sum_{i=1}^{N} -\frac{\hbar^2}{2m_e}\nabla_i^2}_{\substack{\text{electronic}\\ \text{kinetic energy}}} + \underbrace{\frac{1}{2}\sum_{A=1}^{P}\sum_{\substack{B=1\\B\neq A}}^{P}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0\left|\mathbf{R}_A-\mathbf{R}_B\right|}}_{\substack{\text{nuclear-nuclear repulsion}\\ \text{potential energy}}} + \underbrace{\frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\j\neq i}}^{N}\frac{e^2}{4\pi\varepsilon_0\left|\mathbf{r}_i-\mathbf{r}_j\right|}}_{\substack{\text{electron-electron repulsion}\\ \text{potential energy}}} - \underbrace{\sum_{A=1}^{P}\sum_{i=1}^{N}\frac{Z_A e^2}{4\pi\varepsilon_0\left|\mathbf{r}_i-\mathbf{R}_A\right|}}_{\substack{\text{electron-nuclear attraction}\\ \text{potential energy}}}$$

2,3. Write the electronic Schrödinger equation and the nuclear Schrödinger equation for a N-electron P-atom molecule. You may use atomic units.

Electronic Schrödinger Equation:

$$\left(\sum_{i=1}^{N} -\tfrac{1}{2}\nabla_i^2 + \frac{1}{2}\sum_{A=1}^{P}\sum_{\substack{B=1\\B\neq A}}^{P}\frac{Z_A Z_B}{\left|\mathbf{R}_A-\mathbf{R}_B\right|} + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\j\neq i}}^{N}\frac{1}{\left|\mathbf{r}_i-\mathbf{r}_j\right|} + \sum_{A=1}^{P}\sum_{i=1}^{N}\frac{-Z_A}{\left|\mathbf{r}_i-\mathbf{R}_A\right|}\right)\psi_{\text{el}}\left(\mathbf{r}_1\ldots\mathbf{r}_N\left|\mathbf{R}_1\ldots\mathbf{R}_P\right.\right)$$
$$= E\left(\mathbf{R}_1\ldots\mathbf{R}_P\right)\psi_{\text{el}}\left(\mathbf{r}_1\ldots\mathbf{r}_N\left|\mathbf{R}_1\ldots\mathbf{R}_P\right.\right)$$

Nuclear Schrödinger Equation:

$$\left(\sum_{A=1}^{P} -\tfrac{1}{2}\nabla_A^2 + E\left(\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_P\right)\right)\chi_{\text{nuc}}\left(\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_P\right) = E_{\text{total}}\chi_{\text{nuc}}\left(\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_P\right)$$

4. Describe the Born-Oppenheimer approximation *in words,* taking care to make it clear what the fundamental approximation is.

The basic idea is that the electrons move much faster than the nuclei, so that the nuclei are *fixed* from the perspective on the electrons. This motivates writing the wavefunction as a product of an electronic part (which depends on the position of the nuclei, since the electrons adapt to the positions of the nuclei) and a nuclear part (which does not depend on the electronic positions),

$$\Psi_{\text{total}}\left(\mathbf{r}_1,\ldots,\mathbf{r}_N;\mathbf{R}_1,\ldots,\mathbf{R}_P\right) = \psi_{\text{el}}\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\left|\mathbf{R}_1,\ldots,\mathbf{R}_P\right.\right)\chi\left(\mathbf{R}_1,\ldots,\mathbf{R}_P\right)$$

We substitute this into the molecular Schrodinger equation and then *neglect all terms that involve the nuclear momentum/kinetic energy of the electronic wavefunction*. That is, we say that since we *assume* that the nuclei are fixed with respect to the position of electrons, terms like $-i\hbar\nabla_A\psi_{\text{el}}\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\left|\mathbf{R}_1,\ldots,\mathbf{R}_P\right.\right)$ and $-\frac{\hbar^2}{2m_A}\nabla_A^2\psi_{\text{el}}\left(\mathbf{r}_1,\ldots,\mathbf{r}_N\left|\mathbf{R}_1,\ldots,\mathbf{R}_P\right.\right)$ can be set equal to zero. Separation of variables then allows us to write separate Schrödinger equations for the electronic and nuclear wavefunctions.

5. The energy eigenvalues of a 1-electron atom become ______ as the principle quantum number, *n*, increases.

(a) closer together (b) further apart

(using the fact the eigenvalues of the 1-electron atom are $-Z^2/2n^2$ you see, for example for the hydrogen atom, that the energies are $\frac{-1}{2},\frac{-1}{8},\frac{-1}{18},\frac{-1}{32},\frac{-1}{50},\frac{-1}{72},\frac{-1}{98},\ldots$

Name________________________________ Student #__________________________

Bonus: (10 points) What is the normalization constant for the ground state of the hydrogenic atom in atomic units. Remember that in spherical coordinates, an integral of a function over all space has the form

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} f\left(r,\theta,\phi\right) r^2 \sin\theta d\phi d\theta dr \textbf{.}$$

The following integral may be useful,

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \qquad\qquad n = 1, 2, \ldots; a > 0$$

From the form of the wavefunction for the ground state of a 1-electron "hydrogenic" atom with atomic number Z in atomic units,

$$\psi_{\text{1 el atom}}\left(r,\theta,\phi\right) = Ae^{-Zr}$$

the normalization constant can be determined by evaluating the integral

$$1 = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi^*\left(r,\theta,\phi\right)\psi\left(r,\theta,\phi\right) r^2 \sin\theta d\phi d\theta dr$$

$$= \left|A\right|^2 \int_0^\infty \int_0^\pi \int_0^{2\pi} e^{-2Zr} r^2 \sin\theta d\phi d\theta dr$$

The innermost integral is

$$\int_0^{2\pi} d\phi = 2\pi$$

and the next integral is

$$\int_0^\pi \sin\theta d\theta = \left[-\cos\theta\right]_0^\pi = \left(1-\left(-1\right)\right) = 2$$

This gives us the (usual) form for the integration of a spherically symmetric function over all space, namely,

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} f\left(r\right) r^2 \sin\theta d\phi d\theta dr = \int_0^\infty f\left(r\right) 4\pi r^2 dr$$

and in this specific case, the normalization integral is

$$1 = 4\pi\left|A\right|^2 \int_0^\infty e^{-2Zr} r^2 dr$$

$$1 = 4\pi\left(\frac{2!}{\left(2Z\right)^3}\right)\left|A\right|^2$$

$$\left|A\right|^2 = \frac{8Z^3}{8\pi}$$

and the normalization constant is

$$A = \sqrt{\frac{Z^3}{\pi}}$$