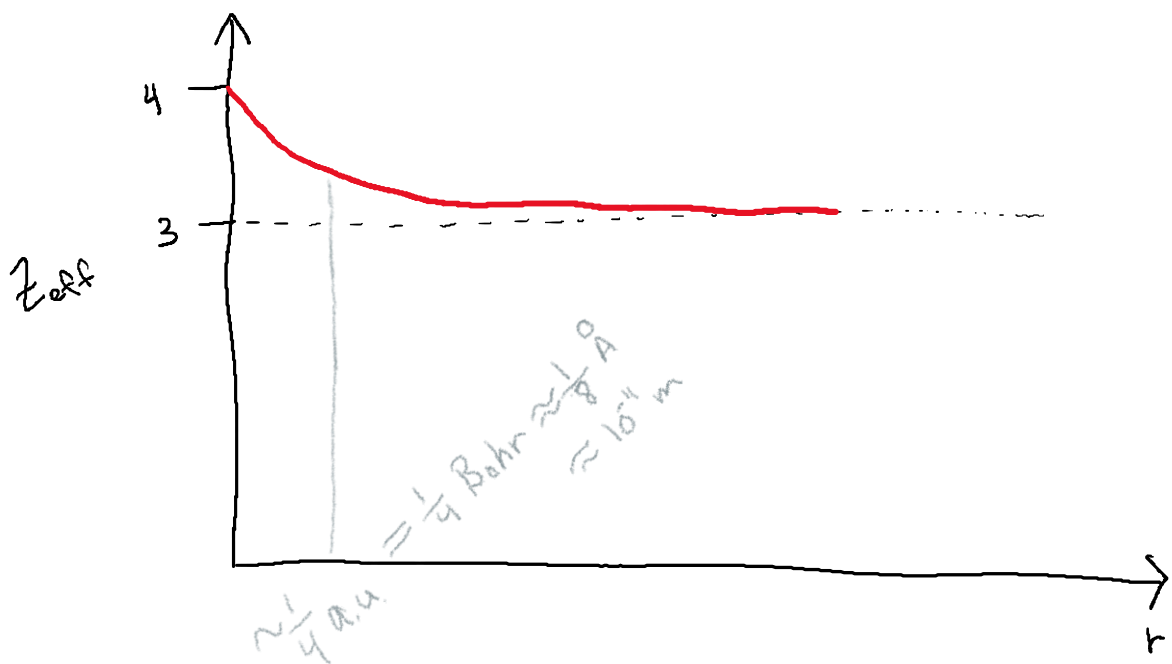
Name________________________________ Student #__________________________

Quiz 13
CHEM 3PA3; Fall 2018

This quiz has 10 problems worth 10 points each. There are 10 bonus points….

1. 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:



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:

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

$$= E\left(\mathbf{R}_1\ldots\mathbf{R}_P\right)\psi_{\text{el}}\left(\mathbf{r}_1\ldots\mathbf{r}_N|\mathbf{R}_1\ldots\mathbf{R}_P\right)$$

Nuclear Schrödinger Equation:

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

Name____________________________________ Student #______________________________

4. What are the term symbols for the [Ar]4s²3d¹4p¹ excited state (Titanium)?

The 3d electron has L = 2 and S = ½ and the 4p electron has L = 1 and S = ½. The possible choices of orbital angular momentum then range from $L = |L_1 - L_2|, \ldots, L_1 + L_2 = 1, 2, 3$ and the choices of spin-angular momentum range from $S = |S_1 - S_2|, \ldots, S_1 + S_2 = 0, 1$.

5. What is the predicted order of the states according to Hund's rules.

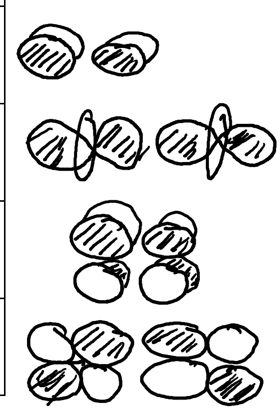
So the states are ${}^3\mathrm{F}, {}^3\mathrm{D}, {}^3\mathrm{P}, {}^1\mathrm{F}, {}^1\mathrm{D}, {}^1\mathrm{P}$ in Hunds rule order. If we add on the J values, we have ${}^3\mathrm{F}_2, {}^3\mathrm{F}_3, {}^3\mathrm{F}_4, {}^3\mathrm{D}_1, {}^3\mathrm{D}_2, {}^3\mathrm{D}_3, {}^3\mathrm{P}_0, {}^3\mathrm{P}_1, {}^3\mathrm{P}_2, {}^1\mathrm{F}_3, {}^1\mathrm{D}_2, {}^1\mathrm{P}_1$.

6. What is the predicted order of states according to the Kutzelnigg-Morgan and Russell-Meggers rules?

According to the Kutzelnigg-Morgan and Russell-Meggers rules, the L = 2 states have odd parity and the L = 1 and L = 3 states have even parity. Moreover, $L_{\text{opt}} = \frac{2+1}{\sqrt{2}} = 2.12$. So the predicted order of states is ${}^1\mathrm{D}, {}^3\mathrm{D}, {}^3\mathrm{F}, {}^3\mathrm{P}, {}^1\mathrm{F}, {}^1\mathrm{P}$.

7-10. For each of the following orbitals, assign a symmetry label $\{\sigma, \pi, \delta, \ldots\}, \{u, g\}, \{+, -\}$. Assume that the orbitals are the atomic orbitals of the left and right atom in the separated-atom limit, and that the molecule is a homonuclear diatomic molecule. Assume that the bond axis is the z axis. Circle whether the orbital is bonding or antibonding.

Orbital	**Symmetry-Label**	**Bonding/Antibonding** (circle one)
$\psi^{(l)}_{2p_y}(\mathbf{r}) + \psi^{(r)}_{2p_y}(\mathbf{r})$	$1\pi_u^-$	**bonding** antibonding
$\psi^{(l)}_{3d_0}(\mathbf{r}) + \psi^{(r)}_{3d_0}(\mathbf{r})$	$6\sigma_g^+$	**bonding** antibonding
$\psi^{(l)}_{3d_{xy}}(\mathbf{r}) + \psi^{(r)}_{3d_{xy}}(\mathbf{r})$	$1\delta_g^-$	**bonding** antibonding
$\psi^{(l)}_{3d_{xz}}(\mathbf{r}) - \psi^{(r)}_{3d_{xz}}(\mathbf{r})$	$5\pi_u^+$	**bonding** antibonding



Bonus (10 points): What is the lowest-energy term symbol for the [Ar]4s²3d⁷ configuration (Cobalt)?

This is the same, essentially, as the Scandium example in quiz #8. The ground-state term is ${}^4\mathrm{F}$. A representative Slater determinant (with maximum $M_L = 3$ and $M_S = \frac{3}{2}$) is $\left| \cdots 3d_{+2}^{\uparrow} 3d_{+2}^{\downarrow} 3d_{+1}^{\uparrow} 3d_{+1}^{\downarrow} 3d_{0}^{\uparrow} 3d_{-1}^{\uparrow} 3d_{-2}^{\uparrow} \right\rangle$. It is a more than half-filled shell so the J-decorated ground-state term is ${}^4\mathrm{F}_{9/2}$.

Name____________________________________ Student #____________________________

Quiz 13
CHEM 3PA3; Fall 2018

This quiz has 10 problems worth 10 points each. There are 10 bonus points….

1. 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 $r \to +\infty$.

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:

Name________________________________ Student #__________________________

4. What are the term symbols for the [Ar]$4s^2 3d^1 4p^1$ excited state (Titanium)?

5. What is the predicted order of the states according to Hund's rules?

6. What is the predicted order of states according to the Kutzelnigg-Morgan and Russell-Meggers rules?

7-10. For each of the following orbitals, assign a symmetry label $\{\sigma,\pi,\delta,\ldots\},\{u,g\},\{+,-\}$. Assume that the orbitals are the atomic orbitals of the left and right atom in the separated-atom limit, and that the molecule is a homonuclear diatomic molecule. Assume that the bond axis is the *z* axis. Circle whether the orbital is bonding or antibonding.

Orbital	**Symmetry-Label**	**Bonding/Antibonding** (circle one)
$\psi_{2p_y}^{(l)}(\mathbf{r})+\psi_{2p_y}^{(r)}(\mathbf{r})$		bonding antibonding
$\psi_{3d_0}^{(l)}(\mathbf{r})+\psi_{3d_0}^{(r)}(\mathbf{r})$		bonding antibonding
$\psi_{3d_{xy}}^{(l)}(\mathbf{r})+\psi_{3d_{xy}}^{(r)}(\mathbf{r})$		bonding antibonding
$\psi_{3d_{xz}}^{(l)}(\mathbf{r})-\psi_{3d_{xz}}^{(r)}(\mathbf{r})$		bonding antibonding

Bonus (10 pts): What is the lowest-energy term symbol for the [Ar]$4s^2 3d^7$ configuration (Cobalt)?