

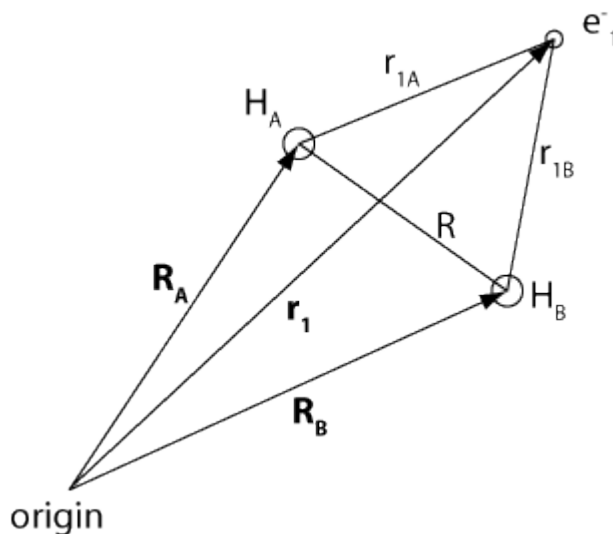
Problem Set 7

Due beginning of class on Friday, March 16

(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)

- For exchange of any two electrons, label each of the following functions as symmetric, antisymmetric, or neither.
 - $f(1)g(2)\alpha(1)\alpha(2)$
 - $f(1)f(2)[\alpha(1)\beta(2)-\beta(1)\alpha(2)]$
 - $f(1)f(2)f(3)\beta(1)\beta(2)\beta(3)$
 - $[f(1)g(2)-g(1)f(2)][\alpha(1)\beta(2)-\alpha(2)\beta(1)]$
- Prove that the maximum in the radial probability distribution, $P_{n,l}(r)$, of a 1s orbital in a hydrogen atom occurs at $r = a_0$.
 - Find $\langle r \rangle$ for a 1s orbital of a hydrogen atom as a function of a_0 . Explain any difference between this result and your result from part (a.).
- The essence of the Born-Oppenheimer Approximation for molecules is that the electrons move much more quickly than the more massive nuclei. Thus, we can fix the internuclear separation, R , and solve the electronic Schrödinger equation. We can then vary R slightly, and solve the electronic Schrödinger equation again for a new set of electronic eigenvalues. By continually varying R and solving the electronic Schrödinger equation, we can build the potential $E(R)$ for the molecule. We will now go through a more formal derivation that will give this result.

Show below is a schematic of the H_2^+ molecule.



where \mathbf{R}_A , \mathbf{R}_B , and \mathbf{r}_I are the coordinates of H_A , H_B , and the electron (vectors are in bold). r_{IA} and r_{IB} are the distances between the electron and each nucleus. R is the distance between the hydrogen nuclei.

- a.) Write down the full Hamiltonian for H_2^+ . Use ∇^2 in the kinetic energy operators. (For example: ∇_A^2)
- b.) Write down the Hamiltonian for the electron of H_2^+ , $H_{el}(\mathbf{r}_I; R)$. (This notation means that R is fixed.) This is called the electronic Hamiltonian. To do this, write down the full Hamiltonian without the kinetic energy terms for the hydrogen nuclei. (We do not include these in the electronic Hamiltonian because the electron moves much more quickly than the nuclei, as stated above. The nuclei are essentially stationary relative to the electron.)
- c.) If we write the total wavefunction as

$$\Psi_{tot}(\mathbf{r}_I, \mathbf{R}_A, \mathbf{R}_B) = \Psi_{el}(\mathbf{r}_I; R) \Psi_n(\mathbf{R}_A, \mathbf{R}_B) \quad \text{Equation 1}$$

we can write the electronic Schrödinger equation as

$$H_{el}(\mathbf{r}_I; R) \Psi_{el}(\mathbf{r}_I; R) = E_{el}(R) \Psi_{el}(\mathbf{r}_I; R) \quad \text{Equation 2}$$

Why is $E_{el}(R)$ a function of R ?

- d.) Using the total Hamiltonian as written in part a.), Eqn 1 for $\Psi_{tot}(\mathbf{r}_I, \mathbf{R}_A, \mathbf{R}_B)$, and Eqn 2, simplify the Schrödinger equation to obtain:

$$\left[-\frac{\hbar^2}{2m_H} (\nabla_A^2 + \nabla_B^2) + E_{el}(R) \right] \Psi_n(\mathbf{R}_A, \mathbf{R}_B) = E \Psi_n(\mathbf{R}_A, \mathbf{R}_B)$$

This is the nuclear Schrödinger equation. Notice that the eigenvalue of the electronic Schrödinger Equation, $E_{el}(R)$, which is a function of R , is now the potential in the nuclear Hamiltonian, which will give us the wavefunctions for rotational and vibrational motion.