

## Homework assignment 2

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### Problem 1: Slater determinants

Let  $\phi_a$ ,  $\phi_b$  and  $\phi_c$  be three eigenfunctions (orbitals) of a one-electron Hamiltonian

$$h(i) = -\frac{\hbar^2 \nabla_i^2}{2m} + V(i)$$

with non-degenerate eigenvalues  $w_a$ ,  $w_b$  and  $w_c$  respectively, i.e.

$$h\phi_a(\vec{r}) = w_a\phi_a(\vec{r}), \quad \text{etc.}$$

(a) How many Slater determinants can be formed to describe the state of a three electron system with only one electron in each of the three different orbitals? (Show symbolically, for example  $|\bar{a}bc\rangle$ ).

(b) Given the total Hamiltonian

$$H = \sum_{i=1}^3 h(i) + \sum_{i=1}^3 \sum_{j<i}^2 \frac{e^2}{r_{ij}}$$

evaluate  $\langle \Psi^{3/2} | H | \Psi^{3/2} \rangle$  where  $|\Psi^{3/2}\rangle$  denotes the  $M_s = \frac{3}{2}$  state. ( $M_s$  is the eigenvalue of  $S_z$ ). Give your answer in terms of the eigenvalues and the Coulomb and exchange integrals, i.e.  $w_a$ ,  $w_b$ ,  $w_c$ ,  $J_{ab}$ ,  $J_{bc}$ ,  $J_{ca}$ ,  $K_{ab}$ ,  $K_{bc}$  and  $K_{ca}$ . Show that your results are consistent with the following rule:

*For a determinantal wave function*

- I. each electron in spatial orbital  $\phi_a$  contributes  $h_{aa} = [a|h|a]$  to the energy;*
- II. each unique pair of electrons contributes  $J_{ab}$  (irrespective of spin) if one of the electrons is in orbital  $\phi_a$  and the other in  $\phi_b$  (a could be the same as b);*
- III. each pair of electrons with parallel spin contributes  $-K_{ab}$  if one of the electrons is in orbital  $\phi_a$  and the other in  $\phi_b$ .*

(c) Using the rules in part (b), give the energy of one of the  $M_s = \frac{1}{2}$  determinants from part (a).

(d) Using the fact that each one of the determinants is an eigenfunction of  $S_z$ , show that  $H$  can only have non-zero matrix elements between determinants with equal  $M_s$  (Note that  $H$  commutes with  $S_z$ ).

### Problem 2: Representation of Slater orbitals in terms of Gaussians

Consider the 1s state of the hydrogen atom described by the wavefunction

$$\Psi_{100}(x, y, z) = \left( \frac{1}{\pi a_0^3} \right) e^{-\sqrt{x^2+y^2+z^2}/a_0}$$

- Plot the wavefunction along the  $x$ -axis going through the nucleus, from  $x = -3\text{\AA}$  to  $x = 3\text{\AA}$ .
- Use Matlab to fit a Gaussian to  $\Psi$  using a least squares procedure. Estimate from the width of the wavefunction a value for  $\alpha$  that is likely to be good. Then, choose a few different values of  $\alpha$  to find a value that is roughly optimal. One reasonable indicator of the goodness of fit is the integral over the squared difference between the wavefunction and the Gaussian. Choose the width that gives the smallest value of this indicator. Plot the best Gaussian fit on top of a plot of  $\Psi$ .
- Now fit  $\Psi$  to a linear combination of three Gaussians, one of them having the ‘near-optimal’ width you found in part (b) and the others having half the width and twice the width. Plot the optimal linear combination of Gaussians on top of a plot of  $\Psi$ .
- [Optional] A non-linear fitting routine is needed to do a full optimization of both the linear combination coefficients and the Gaussian widths in a three Gaussian approximation to the 1s orbital. Find a package for Matlab that can do non-linear least-squares fitting and carry out the optimization for a STO-3G basis set for the 1s orbital of hydrogen.
- Explain why it is advantageous to use the linear combination of Gaussians rather than the exact 1s orbital in calculations of chemical bonding to H-atoms.

### Problem 3: Hartree-Fock estimate of ionization energy

Let the determinant

$$|\Psi_0\rangle = |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2 \dots \psi_{N/2}\bar{\psi}_{N/2}\rangle$$

describe the ground state of a neutral, closed shell  $N$  electron system with energy  $E_N$ .

- A single electron is now removed from orbital  $\psi_i(\vec{r})$ . Give an expression for the ionization energy in terms of  $h_{ii} = (\psi_i|h|\psi_i)$ ,  $J_{ij}$  and  $K_{ij}$ . (That is, find  $E_N - E_{N-1}$ ).
- Give an expression for the double ionization energy, i.e. the energy required to remove two electrons, assuming both come out of the same orbital,  $\psi_i$  (i.e., find  $E_N - E_{N-2}$ ).
- Explain what approximations are being made in the estimates in (a) and (b).