

Lecture 27, April 3, 2006

(Some material in this lecture has been adapted from Cramer, C. J. *Essentials of Computational Chemistry*, Wiley, Chichester: 2002; pp. 116-118.)

**Solved Homework**

In the ground-state He atom at the first step, each electron is assumed to occupy a hydrogenic 1s orbital. Recall that, with  $Z = 2$  for He, this orbital is defined as

$$\psi_{100}(r, \theta, \phi) = \left(\frac{8}{\pi}\right)^{1/2} e^{-2r}$$

The square of this wave function defines the charge cloud that creates the repulsive potential. Thus, at any point  $\mathbf{r}_0$  the total repulsion  $E$  felt by a point charge  $q$  at point  $\mathbf{r}_0$  will be

$$E(\mathbf{r}_0) = q \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{1}{|\mathbf{r} - \mathbf{r}_0|} |\psi_{100}(r, \theta, \phi)|^2 r^2 dr \sin\theta d\theta d\phi$$

where somewhat sloppy notation has been used to try to keep things simpler. The distance between point  $\mathbf{r}_0$  and any point in the integration depends on all three polar coordinates (not just  $r$ ), so the integral is not necessarily easy to solve.

What is easier to notice is that, since the electron we are interested in is itself *also* delocalized (and not a point charge  $q$ ), the total repulsion is a *double* integral, where we integrate over the space of the first electron the repulsion felt by the fractional charge at any point defined by the equation above that involves integrating over the space of the *second* electron. The result is just our old friend the Coulomb integral

$$E = \iint |\psi_{100}(1)|^2 \frac{1}{r_{12}} |\psi_{100}(2)|^2 dr_1 dr_2$$

where each  $dr$  now stands for a complete spherical polar differential volume element. The solution to this integral is fairly painful, but can be achieved through some heroic coordinate transformations. We'll forego the pleasure.

Since 1s orbitals have their maximum amplitudes at the nucleus, electron 1 will be most repelled by electron 2 near the nucleus, and less so further away. So, electron 1 will tend to localize its density further from the nucleus than would be true were electron 2

not to be there (which is what  $\psi_{100}$  assumes, since it is a one-electron orbital, not a two-electron orbital). We've seen this previously in discussion of the variational process where we treated the He atomic number as a parameter and determined it to be 1.69—this drop from 2 causes the electron to localize further away.

Of course, each electron does this to the other, so in the next step, the repulsion near the nucleus felt by each will be reduced (because each electron is now spread out further), and after step 2 the electron will contract back in a bit. Now, at step 3, since charge has reconcentrated near the nucleus, the electronic orbitals will expand out a little bit more, and this will continue in smaller and smaller incremental steps until we declare convergence to have been achieved based on the increment being sufficiently small.

If the original second electron had been in a 2s orbital instead of a 1s, it would have repelled electron 1 considerably less, since it would have much smaller amplitude near the nucleus. The original electron 1 would not have expanded as far outward at step 2, and in the final result we would presumably find electron 1 to have greater density near the nucleus than in the  $1s^2$  case.

### Some Spin Review

The Hartree product wave function fails to be rigorous in two respects. First, it is not antisymmetric. Second, it takes no obvious account of spin.

Recall that all electrons are characterized by a spin quantum number. The electron spin function is an eigenfunction of the operator  $S_z$  and has only two eigenvalues,  $\pm\hbar/2$ ; the spin eigenfunctions are orthonormal and are typically denoted as  $\alpha$  and  $\beta$  (not to be confused with the  $\alpha$  and  $\beta$  of Hückel theory!) The spin quantum number is a natural consequence of the application of relativistic quantum mechanics to the electron (i.e., accounting for Einstein's theory of relativity in the equations of quantum mechanics), as first shown by Dirac. Another consequence of relativistic quantum mechanics is the so-called Pauli exclusion principle, which is usually stated as the assertion that no two electrons can be characterized by the same set of quantum numbers. Thus, in a given MO (which defines all electronic quantum numbers except spin) there are only two possible choices for the remaining quantum number,  $\alpha$  or  $\beta$ , and thus only two electrons may be placed in any MO.

We can account for antisymmetry and spin by formation of determinantal wave functions having spin-orbital elements according to

$$\Psi_{\text{SD}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix} \quad (27-1)$$

where  $N$  is the total number of electrons and  $\chi$  is a spin-orbital, i.e., a product of a spatial orbital and an electron spin eigenfunction. A still more compact notation that finds widespread use is

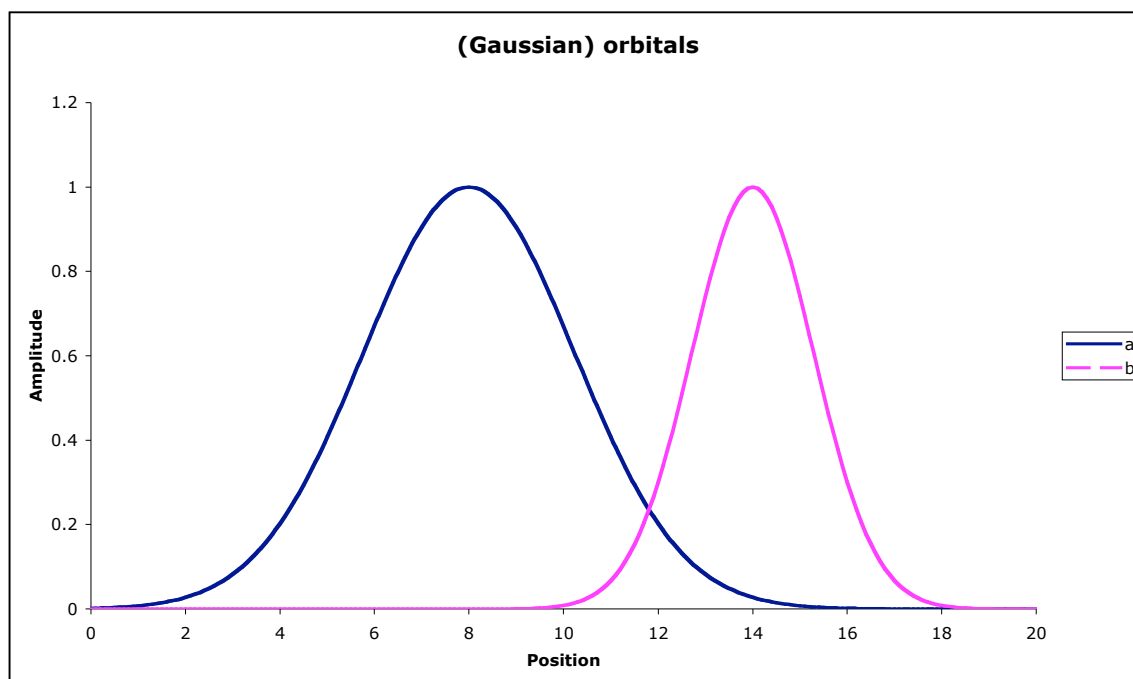
$$\Psi_{\text{SD}} = |\chi_1\chi_2\chi_3\cdots\chi_N\rangle \quad (27-2)$$

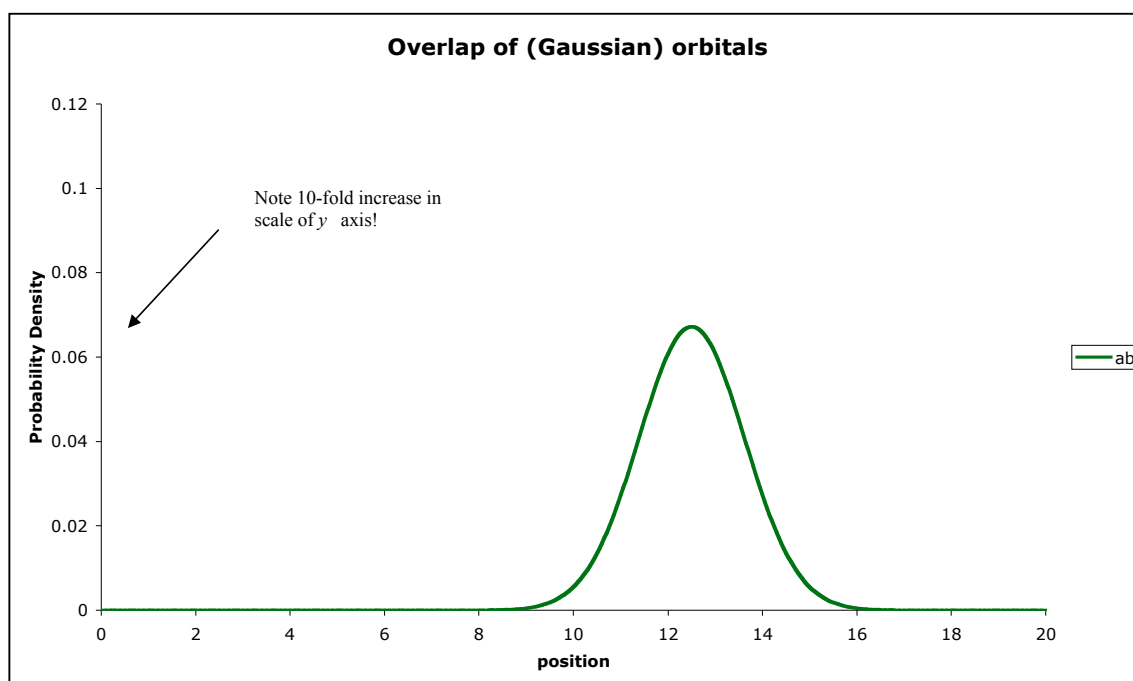
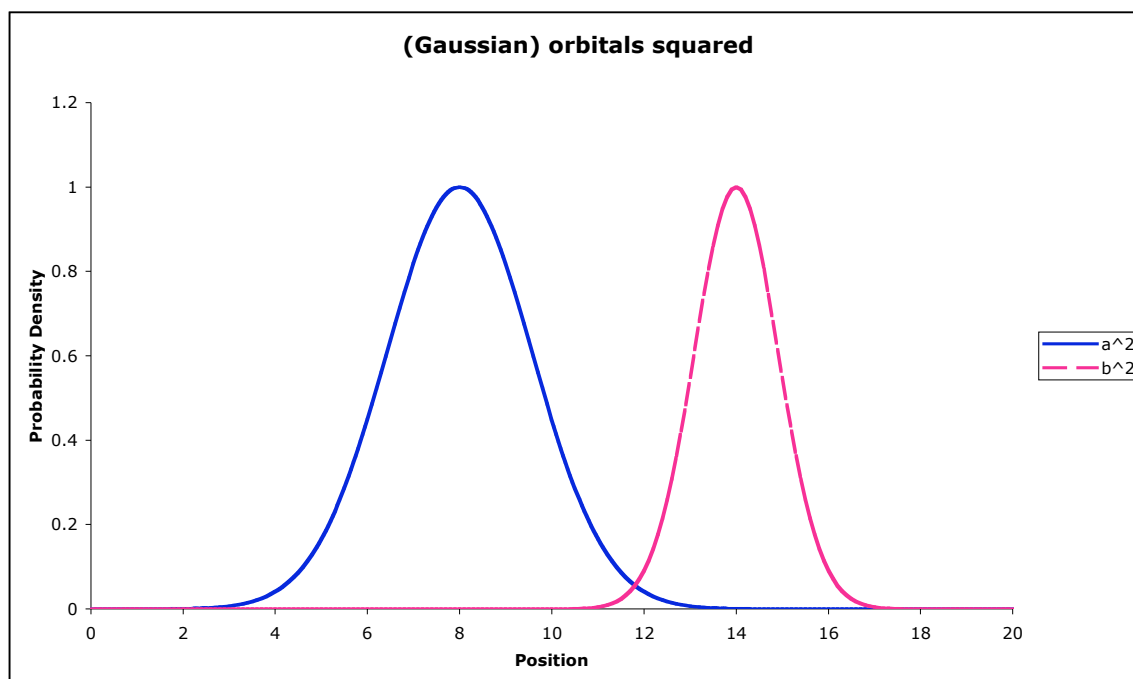
where the prefactor  $(N!)^{-1/2}$  is implicit. Furthermore, if two spin orbitals differ only in the spin eigenfunction (i.e., together they represent a doubly filled orbital) this is typically represented by writing the spatial wave function with a superscript 2 to indicate double occupation. Thus, if  $\chi_1$  and  $\chi_2$  represented  $\alpha$  and  $\beta$  spins in spatial orbital  $\psi_1$ , one would write

$$\Psi_{\text{SD}} = |\psi_1^2\chi_3\cdots\chi_N\rangle \quad (27-3)$$

Perhaps the most important thing to recall about determinantal wave functions is that the evaluation of their energies (as expectation values of the Hamiltonian operator) introduces *exchange* integrals  $K_{ab}$ . The exchange integral differs from the Coulomb integral ( $J_{ab}$ ) insofar as it does not involve the products of square moduli of individual orbitals divided by the distance between points (see homework above for an example), but instead involves the product of one orbital with *another* orbital and a distance operator.

To try to offer a geometric picture, consider the below diagram in one-dimension. Orbitals  $a$  and  $b$  are gaussian functions centered about different points. Shown at top are the orbitals themselves, and immediately below are shown the square moduli of the





orbitals. So, the Coulomb integral may be thought of as parsing over the curve for electron 1 in orbital  $a$ , and at every point along that curve, one runs over all possible points for orbital  $b$  and sums up the product of the amplitudes of the two square moduli ( $a$  held fixed for its own point,  $b$  varying over its whole range) divided by the distance between the fixed  $a$  point and the varying  $b$  point. The double integration follows from

adding all of the sums for all possible points in  $a$  together. One can readily see that if the gaussians become very, very narrow, and fairly far apart, the result is Coulomb's law: the only parts of the double integral that will not be zero for one function or the other will be when they are very near the separation between their maxima, and the total charge is confined in that small region. Because Coulomb's law only drops off as  $1/r$ , significant interaction energies can remain even over fairly large distances.

What about the exchange integral? In this case, we have

$$E = \iint a(1)b(1) \frac{1}{r_{12}} a(2)b(2) dr_1 dr_2 \quad (27-4)$$

so the function we are interested in is  $a$  times  $b$ . If  $a$  and  $b$  don't have much overlap, the product of the two is nearly zero everywhere. Even without doing a double integration dividing by distances between points, one can see that this integral will become small very quickly as the separation between  $a$  and  $b$  increases (see figure above). So, the exchange integral is only very important when  $a$  and  $b$  are quite close to one another. Remember that the exchange integral dictates how much "happier" the system is to have two same-spin electrons close to one another rather than two opposite-spin electrons. Antisymmetry ensures that two same spin electrons can never be *too* close (or the wave function would vanish when the orbitals became the same), but does not require two different-spin electrons to be separated (since they have different spin quantum numbers).

As a final word on this subject, some of you may be wondering why the Coulomb and exchange integrals are not infinite, since it is possible for  $r_{12}$ , the distance between the two electrons, to be zero! The slightly tricky answer is that, as  $r_{12}$  goes to zero, the volume elements in the integration go to zero faster than  $1/r_{12}$  goes to infinity, so no singularity is introduced. Another miracle of quantum mechanics...

## The Hartree-Fock Method

Fock first proposed the extension of Hartree's SCF procedure to Slater determinantal wave functions. Just as with Hartree product orbitals, the Hartree-Fock (HF) MOs can be individually determined as eigenfunctions of a set of one-electron operators, but now the interaction of each electron with the static field of all of the other electrons (this being the basis of the SCF approximation) *includes exchange effects* on the Coulomb repulsion. Some years later, in a paper that was critical to the further development of practical computation, Roothaan described matrix algebraic equations that permitted HF calculations to be carried out using a basis set representation for the MOs. We will forego a formal derivation of all aspects of the HF equations, and simply present them in their typical form for closed-shell singlet systems (i.e., all electrons spin-paired, 2 per occupied orbital) with wave functions represented as a single Slater determinant (which is always possible for a closed-shell wave function). This formalism

is called “restricted Hartree-Fock” (RHF); alternative formalisms are available for other kinds of spin states, but we may not have a chance to get to them.

The one-electron Fock operator is defined for each electron  $i$  as

$$f_i = -\frac{1}{2}\nabla_i^2 - \sum_k^{\text{nuclei}} \frac{Z_k}{r_{ik}} + V_i^{\text{HF}}\{j\} \quad (27-5)$$

where the final term, the HF potential, is  $2J_i - K_i$ , and the  $J_i$  and  $K_i$  operators are defined so as to compute the  $J_{ij}$  and  $K_{ij}$  integrals previously defined above for all other electrons  $j$ . In particular

$$\begin{aligned} J_i \psi_i(i) &= \sum_j^{\text{electrons}} \left\langle \psi_j(j) \left| \frac{1}{r_{ij}} \right| \psi_j(j) \right\rangle \psi_i(i) \\ K_i \psi_i(i) &= \sum_j^{\text{electrons}} \left\langle \psi_j(i) \left| \frac{1}{r_{ij}} \right| \psi_j(j) \right\rangle \psi_i(j) \end{aligned} \quad (27-6)$$

At first glance, these operators should look a bit strange. The Dirac brackets seem to involve the coordinates of two electrons,  $i$  and  $j$ , but there are not wave functions and their complex conjugates for both electrons inside the brackets. However, if we left multiply by the HF orbital  $\psi_i$  for the  $i$ th electron and then integrate, we have the proper results

$$\begin{aligned} \int \psi_i(i) J_i \psi_i(i) dr_i &= \int \psi_i(i) \sum_j^{\text{electrons}} \left\langle \psi_j(j) \left| \frac{1}{r_{ij}} \right| \psi_j(j) \right\rangle \psi_i(i) dr_i \\ &= \sum_j^{\text{electrons}} \left\langle \psi_i(i) \psi_j(j) \left| \frac{1}{r_{ij}} \right| \psi_i(i) \psi_j(j) \right\rangle \\ &= \sum_j^{\text{electrons}} J_{ij} \\ \int \psi_i(i) K_i \psi_i(i) dr_i &= \int \psi_i(i) \sum_j^{\text{electrons}} \left\langle \psi_j(i) \left| \frac{1}{r_{ij}} \right| \psi_j(j) \right\rangle \psi_i(j) dr_i \\ &= \sum_j^{\text{electrons}} \left\langle \psi_i(i) \psi_j(j) \left| \frac{1}{r_{ij}} \right| \psi_i(j) \psi_j(i) \right\rangle \\ &= \sum_j^{\text{electrons}} K_{ij} \end{aligned} \quad (27-7)$$

To determine the MOs using the Roothaan approach, we follow a procedure analogous to that previously described for Hückel theory. First, given a set of  $N$  basis functions, we solve the secular equation

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \cdots & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \cdots & F_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ F_{N1} - ES_{N1} & F_{N2} - ES_{N2} & \cdots & F_{NN} - ES_{NN} \end{vmatrix} = 0 \quad (27-8)$$

to find its various roots  $E_j$ . In this case, the values for the matrix elements  $F$  and  $S$  are all computed explicitly. For each root, there will be a solution to the linear equations defined by the variational theorem and solving those equations will give us coefficients for writing an MO with that energy as a linear combination of the basis functions.

Matrix elements  $S$  are overlap matrix elements we have seen before. For a general matrix element  $F_{\mu\nu}$  (we here adopt a convention that basis functions are indexed by lower-case Greek letters, while MOs are indexed by lower-case Roman letters) we compute

$$\begin{aligned} F_{\mu\nu} = & \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle \\ & + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[ (\mu\nu | \lambda\sigma) - \frac{1}{2} (\mu\lambda | \nu\sigma) \right] \end{aligned} \quad (27-9)$$

The kinetic energy and nuclear attraction terms are so-called one-electron integrals (because integration is over a single set of spherical polar coordinates for a single electron). The notation  $(\mu\nu | \lambda\sigma)$  implies the two-electron integral

$$(\mu\nu | \lambda\sigma) = \iint \phi_\mu(1)\phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda(2)\phi_\sigma(2) d\mathbf{r}(1)d\mathbf{r}(2) \quad (27-10)$$

where  $\phi_\mu$  and  $\phi_\nu$  represent the probability density of one electron and  $\phi_\lambda$  and  $\phi_\sigma$  the other. The exchange integrals  $(\mu\lambda | \nu\sigma)$  are preceded by a factor of 1/2 because they are limited to electrons of the same spin while Coulomb interactions are present for any combination of spins.

The final sum in eq. 27-9 weights the various so-called “four-index integrals” by elements of the “density matrix”  $\mathbf{P}$ . This matrix in some sense describes the degree to which individual basis functions contribute to the many-electron wave function, and thus indicates how energetically important the Coulomb and exchange integrals should be (i.e., if a basis function fails to contribute in a significant way to any of the occupied MOs, clearly integrals involving that basis function should be of no energetic importance in the wave function). The elements of  $\mathbf{P}$  are computed as

$$P_{\lambda\sigma} = 2 \sum_i^{\text{occupied}} a_{\lambda i} a_{\sigma i} \quad (27-11)$$

where the coefficients  $a_{\zeta i}$  specify the (normalized) contribution of basis function  $\zeta$  to MO  $i$  and the factor of two appears because with RHF theory we are considering only singlet wave functions in which all orbitals are doubly occupied.

At this stage, we have defined how to go about computing each term appearing in the Hartree-Fock secular determinant. Next lecture will focus on the individual terms a bit more closely.

### Homework

To be solved in class:

The matrix element  $F_{\mu\nu}$  may be either a diagonal element ( $\mu=\nu$ ) or an off-diagonal element ( $\mu\neq\nu$ ). Will the kinetic energy term be larger for a diagonal element, or an off-diagonal element? Why? What about the nuclear attraction term?

To be turned in for possible grading Apr. 7:

None -- relax for two days (but *do* the non-graded problem above! It's conceptual.)