

Lecture 28, April 5, 2006

(Some material in this lecture has been adapted from Cramer, C. J. *Essentials of Computational Chemistry*, Wiley, Chichester: 2002; pp. 118-119, 154-158.)

Solved Homework

Consider the diagonal and off-diagonal kinetic energy matrix elements

$$T_{\mu\mu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \mu \right\rangle \quad T_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 \right| \nu \right\rangle$$

Let's think about what the Laplacian operator does to the function on which it is operating. It reports back the sum of second derivatives in all coordinate directions. That is, it is a measure of how fast the slope of the function is changing in various directions. If two functions μ and ν are far apart, then since good basis functions go to zero at least exponentially fast with distance, ν is likely to be very flat where μ is large. The second derivative of a flat function is zero. So, every point in the integration will be roughly the amplitude of μ times zero, and not much will accumulate. For the diagonal element, on the other hand, the interesting second derivatives will occur where the function has *maximum* amplitude (amongst other places) so the accumulation should be much larger. Thus, we expect diagonal elements in this case to be larger than off-diagonal elements.

Analogous arguments can be made for the nuclear attraction integrals.

$$V_{\mu\mu} = \left\langle \mu \left| - \sum_k^{\text{nuclei}} \frac{Z_k}{r_k} \right| \mu \right\rangle \quad V_{\mu\nu} = \left\langle \mu \left| - \sum_k^{\text{nuclei}} \frac{Z_k}{r_k} \right| \nu \right\rangle$$

The $1/r$ operator acting on ν will ensure that the largest contribution to the overall integral will come from the nucleus k on which basis function ν resides. Unless μ also has significant amplitude around that nucleus, it will multiply the result by roughly zero and the whole integral will be small. In this case, however, it is conceivable (i) that off-diagonal elements involving $Z=100$ might be larger than diagonal elements about $Z=1$ and (ii) that off-diagonal elements involving two basis functions on the *same* nuclear center might compete with diagonal elements involving a more diffuse basis function on that center (e.g., a 1s2s interaction on the same atom might be larger than a 5f interaction with itself, since the latter is so spread out that its amplitude isn't very large anywhere).

The $2J - K$ terms are somewhat more subtle to evaluate, but it will still generally be the case that diagonal terms will generate larger magnitudes than off-diagonal terms. We will not explore the point closely.

The Hartree-Fock Self-Consistent Field Procedure

To find the HF MOs we need to solve the HF secular determinant

$$\begin{vmatrix} F_{11} - ES_{11} & F_{12} - ES_{12} & \cdots & F_{1N} - ES_{1N} \\ F_{21} - ES_{21} & F_{22} - ES_{22} & \cdots & F_{2N} - ES_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ F_{N1} - ES_{N1} & F_{N2} - ES_{N2} & \cdots & F_{NN} - ES_{NN} \end{vmatrix} = 0 \quad (28-1)$$

and find its various roots. We know that we can compute overlap integrals and that Fock matrix elements are defined by

$$F_{\mu\nu} = \left\langle \mu \left| -\frac{1}{2}\nabla^2 \right| \nu \right\rangle - \sum_k^{\text{nuclei}} Z_k \left\langle \mu \left| \frac{1}{r_k} \right| \nu \right\rangle + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\lambda | \nu\sigma) \right] \quad (28-2)$$

So, now for the tricky part.

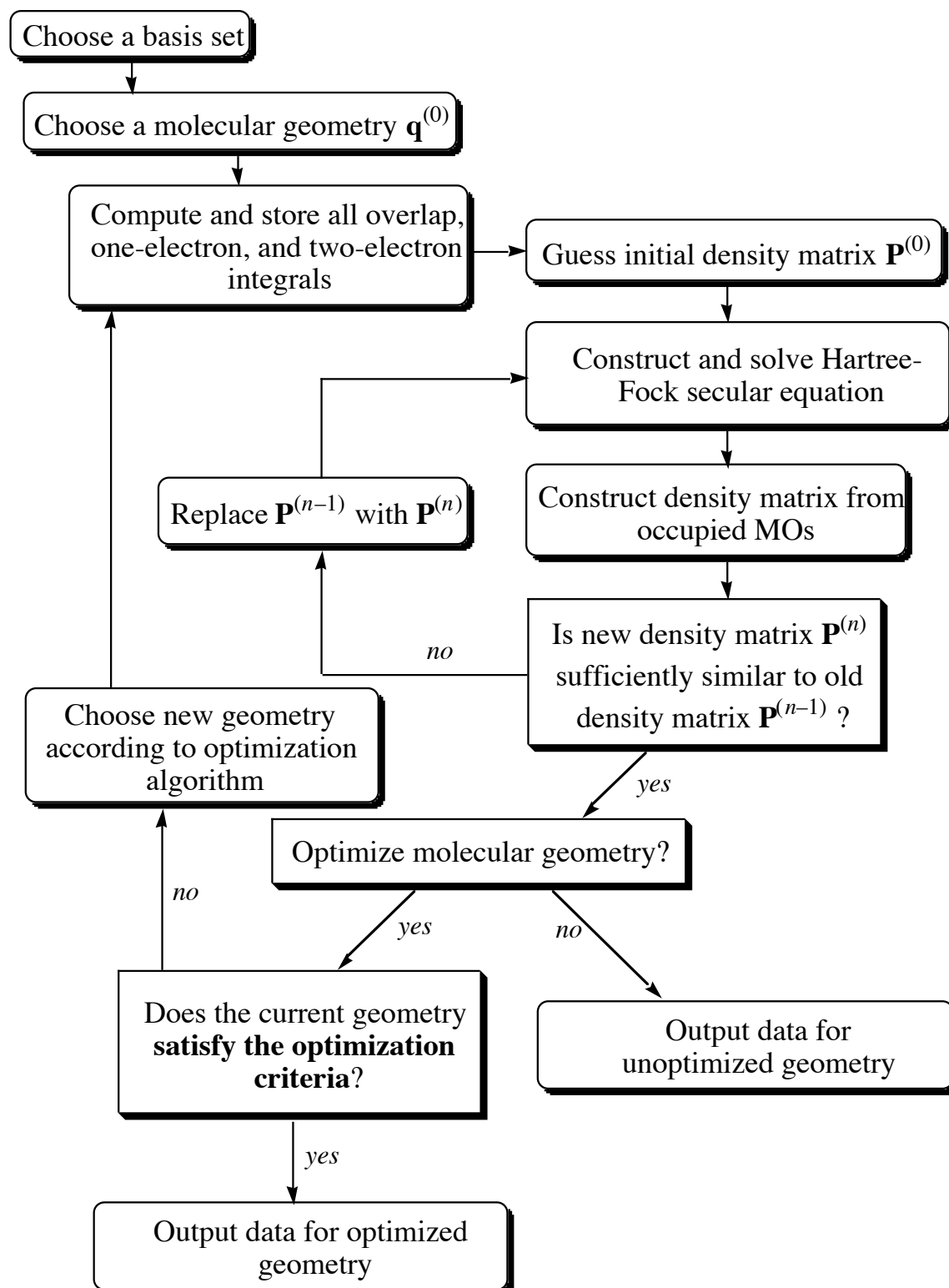
Remember that the density matrix elements appearing in eq. 28-2 are defined as

$$P_{\lambda\sigma} = 2 \sum_i^{\text{occupied}} a_{\lambda i} a_{\sigma i} \quad (28-3)$$

where the a values are the coefficients of the basis functions in the occupied molecular orbitals.

But, the whole point of solving the secular equation is to find those coefficients. So, if we don't know them already, how can we compute the matrix elements, and if we do know them already, why are we doing this in the first place?

This is, of course, the same paradox we saw in the Hartree formalism. And, just as in the Hartree method, the HF method follows a self-consistent field (SCF) procedure, where first we *guess* the orbital coefficients (e.g., from an effective Hamiltonian method, like Hückel theory or a modification thereof) and then we *iterate* to convergence. The full process is described schematically by the flow-chart on the next page. The flow chart includes consideration of optimizing the geometry, but we'll ignore that for now.



After convergence of the MOs, one can compute the HF energy by evaluating the Hamiltonian operator for the HF determinant (the determinant will be formed in the usual

way given all the occupied orbitals to enforce antisymmetry). There is, however, a slightly easier way, too. If we think about the Fock operator for a particular electron, it is, remember

$$f_i = -\frac{1}{2}\nabla_i^2 - \sum_k^{\text{nuclei}} \frac{Z_k}{r_{ik}} + V_i^{\text{HF}}\{j\} \quad (28-4)$$

It only operates on an electron in the i th orbital, so if we take the expectation value of the Fock operator over that orbital—call it ε_i —it represents the total energy of an electron in that orbital. eq. 28-4 includes the attraction of an electron in the orbital to all the nuclei, its kinetic energy, and its repulsion with all the other electrons.

So, if we add up all the ε values for all of the occupied orbitals and double that (because in restricted HF we have two electrons in every orbital), we'll have included all of the physical contributions to the energy. However, we'll have *overcounted* electron-electron repulsion. That's because for an electron in orbital 1, we evaluate the repulsion that electron feels from an electron in orbital 2 (and 3, and 4, etc.) But, when we go and consider the electron in orbital 2 (and 3, and 4, etc.) we account for that interaction again in dictating the energy of electron 2 (etc.) So, we double count all of the electron repulsions. Thus, an alternative way of computing the total energy is to add up all of the individual orbital energies and deduct half of the total electron repulsion energy (cf. eq. 26-8). That is

$$E_{\text{HF}} = \langle \Psi^{\text{HF}} | H | \Psi^{\text{HF}} \rangle = 2 \sum_i^{\text{occupied}} \varepsilon_i - \sum_{i,j}^{\text{occupied}} 2J_{ij} - K_{ij} \quad (28-5)$$

Hartree-Fock theory as constructed using the Roothaan approach is quite beautiful in the abstract. This is not to say, however, that it does not suffer from certain chemical and practical limitations. It's chief chemical limitation is the one-electron nature of the Fock operators. Other than exchange, all electron correlation is ignored. It is, of course, an interesting question to ask just how important such correlation is for various molecular properties, and we will examine that later on.

Furthermore, from a practical standpoint, HF theory posed some very challenging technical problems to early quantum chemists. One problem was choice of a basis set. The LCAO approach using hydrogenic orbitals remains attractive in principle, however, this basis set requires numerical solution of the four-index integrals appearing in the Fock matrix elements, and that is a very tedious process (no analytic solution has yet been found). Moreover, the *number* of four-index integrals is daunting. Since each index runs over the total number of basis functions, there are in principle N^4 total integrals to be evaluated, and this quartic scaling behavior with respect to basis-set size proves to be the bottleneck in HF theory applied to essentially any molecule.

Historically, two philosophies began to emerge at this stage with respect to how best to make further progress. The first philosophy might be summed up as follows: The

HF equations are very powerful but still, after all, chemically flawed since they ignore electron-electron correlation. Thus, other approximations that may be introduced to simplify their solution, and possibly at the same time improve their accuracy (by some sort of parameterization to reproduce key experimental quantities), are well justified. Many quantum chemists continue to be guided by this philosophy today, and it underlies the motivation for so-called “semiempirical” MO theories, which, alas, we lack time to touch upon.

The second philosophy essentially views HF theory as a stepping stone on the way to *exact* solution of the Schrödinger equation. HF theory provides a very well defined energy, one which can be converged in the limit of an *infinite* basis set, and the difference between that converged energy and reality is the electron correlation energy (ignoring relativity, spin-orbit coupling, etc.). It was anticipated that developing the technology to achieve the HF limit *with no further approximations* would not only permit the evaluation of the chemical utility of the HF limit, but also probably facilitate moving on from that low-altitude base camp to the Schrödinger equation summit. Such was the foundation for further research on “*ab initio*” (Latin for “from the beginning”) HF theory. Along the way it became clear that, perhaps surprisingly, HF energies could be chemically useful. Typically their utility was manifest for situations where the error associated with ignoring the correlation energy could be made unimportant by virtue of comparing two or more systems for which the errors could be made to cancel. In any case, we will examine *ab initio* HF theory next.

Gaussian Orbitals as Basis Functions

The basis set is the set of mathematical functions from which the wave function is constructed. As detailed in this and earlier lectures, each MO in HF theory is expressed as a linear combination of basis functions, the coefficients for which are determined from the iterative solution of the HF SCF equations (as flowcharted above). The full HF wave function is expressed as a Slater determinant formed from the individual occupied MOs. In the abstract, the HF limit is achieved by use of an *infinite* basis set, which necessarily permits an optimal description of the electron probability density. In practice, however, one cannot make use of an infinite basis set. Thus, much work has gone into identifying mathematical functions that allow wave functions to approach the HF limit arbitrarily closely in as efficient a manner as possible.

Efficiency in this case involves three considerations. As noted above, in the absence of additional simplifying approximations like those present in semiempirical theory, the number of two-electron integrals increases as N^4 where N is the number of basis functions. So, keeping the total number of basis functions to a *minimum* is computationally attractive. In addition, however, it can be useful to choose basis set functional forms that permit the various integrals appearing in the HF equations to be evaluated in a *computationally* efficient fashion. Thus, a larger basis set can still represent a computational improvement over a smaller basis set *if* evaluation of the greater number of integrals for the former can be carried out faster than for the latter.

Finally, the basis functions must be chosen to have a form that is useful in a chemical sense. That is, the functions should have large amplitude in regions of space where the electron probability density (the wave function) is also large, and small amplitudes where the probability density is small. The simultaneous optimization of these three considerations is at the heart of basis set development.

We previously derived, by solution of the one-electron-atom Schrödinger equation, hydrogenic orbitals; recall that they are characterized by exponential decay that goes as the first power of the radial distance from the atom on which they are centered. In quantum calculations, such orbitals are usually called “Slater”-type orbitals (STOs, named for the same Slater who lent his name to the determinantal wave function). While STOs have the attractive feature that they are based on hydrogenic atomic orbitals, in *ab initio* HF theory they suffer from a fairly significant limitation. There is no analytical solution available for the general four-index integral (eq. 27-10) when the basis functions are STOs. The requirement that such integrals be solved by numerical methods severely limits their utility in molecular systems of any significant size.

In 1950, Boys proposed an alternative to the use of STOs. All that is required for there to be an analytical solution of the general four-index integral formed from such functions is that the radial decay of the STOs be changed from e^{-r} to e^{-r^2} . That is, the AO-like functions are chosen to have the form of a gaussian function. The general functional form of a *normalized* gaussian-type orbital (GTO) in atom-centered cartesian coordinates is

$$\phi(x, y, z; \alpha, i, j, k) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \frac{[(8\alpha)^{i+j+k} i! j! k!]}{[(2i)!(2j)!(2k)!]}^{1/2} x^i y^j z^k e^{-\alpha(x^2+y^2+z^2)} \quad (28-6)$$

where α is an exponent controlling the width of the GTO, and i, j , and k are non-negative integers that dictate the nature of the orbital in a cartesian sense.

In particular, when all three of these indices are zero, the GTO has spherical symmetry, and is called an s-type GTO. When exactly one of the indices is one, the function has axial symmetry about a single cartesian axis and is called a p-type GTO. There are three possible choices for which index is one, corresponding to the p_x , p_y , and p_z orbitals. When the sum of the indices is equal to two, the orbital is called a d-type GTO, etc.

Although they are convenient from a computational standpoint, GTOs have specific features that do diminish their utility as basis functions. One issue of key concern is the shape of the radial portion of the orbital. For s type functions, GTOs are smooth and differentiable at the nucleus ($r = 0$), but real hydrogenic AOs have a cusp (see Figure at end of Lecture 19). In addition, all hydrogenic AOs have a radial decay that is exponential in r while the decay of GTOs is exponential in r^2 ; this results in too rapid a reduction in amplitude with distance for the GTOs.

As we saw previously in discussing variational atomic calculations, in order to combine the best feature of GTOs (computational efficiency) with that of STOs (proper radial shape), most of the first basis sets developed with GTOs used them as building blocks to approximate STOs. That is, the basis functions φ used for SCF calculations were not individual GTOs, but instead a linear combination of GTOs fit to reproduce as accurately as possible a STO, i.e.,

$$\varphi(x, y, z; \{\alpha\}, i, j, k) = \sum_{a=1}^M c_a \phi_a(x, y, z; \alpha_a, i, j, k) \quad (28-7)$$

where M is the number of gaussians used in the linear combination, and the coefficients c are chosen to optimize the shape of the basis function sum and ensure normalization (perhaps by variational calculations on the atom, as we did earlier in the course). When a basis function is defined as a linear combination of gaussians, it is referred to as a “contracted” basis function, and the individual gaussians from which it is formed are called “primitive” gaussians. Thus, in a basis set of contracted GTOs, each basis function is defined by the contraction coefficients c and exponents α of each of its primitives. The “degree of contraction” refers to the total number of primitives used to make all of the contracted functions, as described in more detail below. Contracted GTOs when used as basis functions continue to permit analytical evaluation of all of the four-index integrals.

Optimal contraction coefficients and exponents for mimicking STOs with contracted GTOs have been developed for a large number of atoms in the periodic table using different choices of M in eq. 28-7. These different basis sets are called STO-MG, for “Slater-Type Orbital approximated by M Gaussians”. Obviously, the more primitives that are employed, the more accurately a contracted function can be made to match a given STO. However, note that a four-index two-electron integral becomes increasingly complicated to evaluate as each individual basis function is made up of increasingly many primitive functions, according to

$$\begin{aligned} (\mu\nu|\lambda\sigma) &= \int \varphi_\mu(1)\varphi_\nu(1) \frac{1}{r_{12}} \varphi_\lambda(2)\varphi_\sigma(2) dr_1 dr_2 \\ &= \int \sum_{a_\mu=1}^{M_\mu} c_{a_\mu} \phi_{a_\mu}(1) \sum_{a_\nu=1}^{M_\nu} c_{a_\nu} \phi_{a_\nu}(1) \frac{1}{r_{12}} \sum_{a_\lambda=1}^{M_\lambda} c_{a_\lambda} \phi_{a_\lambda}(2) \sum_{a_\sigma=1}^{M_\sigma} c_{a_\sigma} \phi_{a_\sigma}(2) dr_1 dr_2 \quad (28-8) \\ &= \sum_{a_\mu=1}^{M_\mu} \sum_{a_\nu=1}^{M_\nu} \sum_{a_\lambda=1}^{M_\lambda} \sum_{a_\sigma=1}^{M_\sigma} c_{a_\mu} c_{a_\nu} c_{a_\sigma} c_{a_\lambda} \int \phi_{a_\mu}(1)\phi_{a_\nu}(1) \frac{1}{r_{12}} \phi_{a_\lambda}(2)\phi_{a_\sigma}(2) dr_1 dr_2 \end{aligned}$$

The optimum combination of speed and accuracy (when comparing to calculations using STOs) was achieved for $M=3$. The figure at the end of Lecture 19 compares a 1s function using the STO-3G formalism to the corresponding STO and shows also the 3 primitives from which the contracted basis function is constructed. STO-3G basis functions have been defined for most of the atoms in the periodic table.

Gaussian functions have another feature that would be undesirable if they were to be used *individually* to represent atomic orbitals: they fail to exhibit *radial* nodal behavior! That is, no choice of variables permits eq. 28-6 to mimic a 2s orbital, which is negative near the origin and positive beyond a certain radial distance. Use of a contraction scheme, however, alleviates this problem; contraction coefficients c in eq. 28-7 can be chosen to have either negative or positive sign, and thus fitting to functions having radial nodal behavior poses no special challenges. To make a 2s function you would simply subtract a tighter gaussian from a looser one, in which case it would indeed be negative near the nucleus and positive further away.

Homework

To be solved in class:

Consider the water molecule. If we decide to do a calculation on water and use the STO-3G basis set, how many contracted basis functions will we need in order to minimally represent the total number of atomic orbitals spanned by the core and valence electrons of the oxygen atom and the two hydrogen atoms? How many one-electron integrals will there be that require evaluation? How many two-electron integrals will require evaluation? In each of the last two cases, how many *primitive* integrals will need to be evaluated? Do you see anything that makes the workload slightly less onerous than your formal analysis? How many occupied orbitals will there be in the final Slater determinant?

To be turned in for possible grading Apr. 7:

Repeat the above problem but now for phosphine (PH_3) instead of water.