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Local orbital eigenvalues and basis set balance

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Consideration of the chemical potential of an electron in a wavefunction suggests that a quantity called the local orbital eigenvalue and its variation in space provides a method of testing the balance of a basis set as a function of spatial position. The Hartree–Fock method as applied to the helium and neon atoms is used as an example.

Key words: Basis sets — Orbital eigenvalues — Density functional

The chemical potential of the electrons in an atom or molecule has been defined using density functional theory. Hohenberg and Kohn showed [1], in principle at least, that the energy is a functional of the ground state electron density $E[\rho]$. They also proved the existence of a variational condition on $E[\rho]$. The chemical potential μ is defined as the functional derivative

$$\mu = (\delta E/\delta\rho)_v \tag{1}$$

(with the external potential v held fixed). One consequence of density functional theory is that μ is a constant, invariant with respect to position, in any electronic system [1, 2]. That is, the energy change resulting from an infinitesmal addition of electron density is the same regardless of where in space that density is added. Notice that this must be the case for the exact density; if it were not, the energy could be lowered by a redistribution of electron density. This spatial invariance is similar to the invariance of the local energy defined as

$$E = (H\Psi)/\Psi. \tag{2}$$

If the Schrödinger equation is satisfied exactly, the local energy defined above will be constant in configuration space.

The chemical potential and its features have also been studied in wavefunction theory [3]. If the energy is considered to be a functional of the natural orbitals and occupation numbers of some system $E[\chi_i, n_i]$, the chemical potential (for the exact natural orbitals and occupation numbers) is the same for each of those orbitals. That is

$$\mu = (\partial E/\partial n_i)\chi_k, n_j \quad \text{for all } i \text{ and } k \text{ with } j \neq i. \tag{3}$$

One important feature of an exact wavefunction written in terms of the natural orbitals is that all the occupation numbers turn out to be less than 1.0; hence they need not be constrained from exceeding 1.0 in order to satisfy the Pauli Principle. The equal orbital chemical potential theorem requires this situation. For approximate wavefunctions which involve relatively few orbitals and configurations, the orbital occupation numbers must be constrained to be $n_i \leq 1$ in order to avoid violating the Pauli Principle. The addition of these constraints invalidates the proof of Parr et al. [3], and the energy of such a wavefunction can have a different sensitivity with respect to the occupancy of the various orbitals. In the Hartree-Fock method, this is equivalent to stating that different orbitals can have different eigenvalues because

$$\varepsilon_i = \partial E/\partial n_i. \tag{4}$$

In many wavefunction methods, the total energy is written as a functional of the occupied orbitals ϕ_i and perhaps some variable occupation numbers. Typically the oribtals are optimized by taking the variation of the total energy with respect to an arbitrary change in the orbitals. That is the functional derivative $\delta E/\delta\phi_i$. The resulting variation equation can be manipulated into eigenvalue equations such as $H_i\phi_i = \varepsilon_i\phi_i$ where H_i is some effective Hamiltonian. The simplest example is the Hartree-Fock method in which (for a closed shell) the energy is the functional

$$E[\phi_i] = 2\sum_i \langle\phi_i|h|\phi_i\rangle + \sum_{i,j} (2\langle\phi_i\phi_j \mid \phi_i\phi_j\rangle - \langle\phi_i\phi_j \mid \phi_j\phi_i\rangle) \tag{5}$$

In this case each effective Hamiltonian turns out to be the same, and is called the Fock operator

$$F = H_i = -0.5\nabla^2 - \sum_a Z_a/r_a + \sum_j (2J_j - K_j) \tag{6}$$

In the standard LCAO expansion of the molecular orbitals, the quality of the solution of the Fock eigenvalue equation $F\phi_i = \varepsilon_i\phi_i$ typically depends only on the quality of the basis set used. Usually, a negligible numerical error exists in the integral evaluation or matrix manipulations. The eigenvalue itself can be evaluated as the average $\langle\phi_i|F|\phi_i\rangle$. However, consider dividing the eigenvalue equation by the eigenfunction ϕ_i.

$$e_i(\vec{r}) = (F\phi_i)/\phi_i \tag{7}$$

is a sort of local energy analog for the eigenvalue. This quantity could be named the orbital chemical potential, but we prefer to call it the local eigenvalue. The exact solution to the Hartree-Fock problem must yield local eigenvalues that are constant in space. Such will not be true in any actual LCAO approximate solution to the problem, and the variation of the expression $(F\phi_i)/\phi_i$ will be a measure of the relative quality of the solution for that particular orbital.

Written out in detail for the Hartree-Fock method as an example, the local eigenvalue is

$$e_i(\vec{r}) = -0.5(\nabla^2\phi_i)/\phi_i - \sum_a Z_a/r + \sum_j \{2J_j - (K_j\phi_i)/\phi_i\} \tag{8}$$

where

$$J_j(\vec{r}_1) = \int dV_2 \frac{|\phi_j(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} \tag{9}$$

and

$$K_j(\vec{r}_1) = \int dV_2 \phi_j^*(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} P_{12}\phi_j(\vec{r}_2) \tag{10}$$

are the usual coulomb and exchange operators. The evaluation of these terms requires nothing worse than some three-center nuclear attraction types of integrals.

Detailed inspection of Eq. (8) near the orbital node provides the condition of ϕ_i in that region. The expression

$$\nabla^2\phi_i(\vec{r}_1) + \sum_j \int \phi_j^*(\vec{r}_2)\phi_i(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} dV_2 \phi_j(\vec{r}_1) \tag{11}$$

must approach zero at least as rapidly as ϕ_i does. Because this condition depends on all the occupied orbitals, it does not reduce to a general helpful result. One would expect that roundoff error might cause the $e_i(\vec{r})$ to vary somewhat near nodes in the eigenfunction, but elsewhere, a changing value for $e_i(\vec{r})$ implies a difference in basis set quality.

A quantitative overall measure of the deviation of the local eigenvalue could be a useful item. The most appropriate quantity is a root mean square average of the difference of $e(\vec{r})$ from the orbital energy ε; call it Δ.

$$\Delta = \left\{ \int |\phi(\vec{r})|^2 [e(\vec{r}) - \varepsilon]^2 \, dV \right\}^{1/2}. \tag{12}$$

It seems reasonable to include the orbital density as a weight factor in this integrand to emphasize the most important region of space.

Hartree-Fock solutions for the helium atom provide a simple example to illustrate the usefulness of this method for testing basis sets. We have evaluated $e(r)$ for three different basis sets for helium. First the hydrogenic (exponent = 2) orbital; second the optimized ($\zeta = 1.6875$) single-zeta orbital; and finally the optimized double-zeta wavefunction of Huzinaga [4]. All three are displayed in Fig. 1 where the superiority of Huzinaga's basis set is clearly evident. Only in a very small region near the nucleus does it display noticeable variation in its local eigenvalue. Closer inspection does show a small variation at larger r.

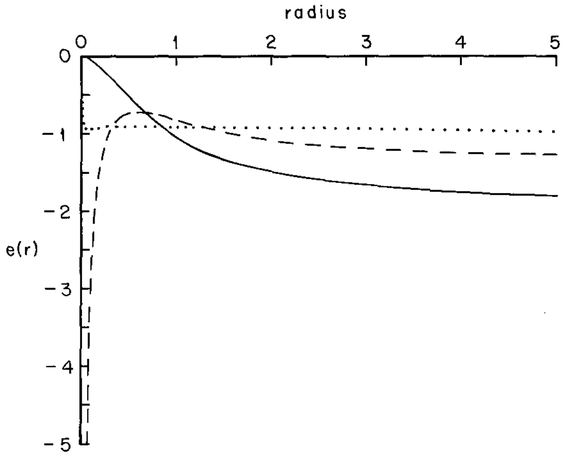

Fig. 1. The local eigenvalue (in atomic units) for the helium atom is shown for three basis sets: hydrogenic (——), optimized single-zeta (- - -), and optimized double-zeta (· · · ·)

The root mean square deviation of the local eigenvalue for helium is 0.383 (in atomic units) for the hydrogenic wavefunction. It improves only to 0.380 for the optimum single-zeta orbital. For the optimum double-zeta basis set, this quantity is very small, $\Delta = 0.0053$; as implied by the plot in Fig. 1, the double-zeta basis gives an excellent description of the Hartree–Fock orbital in helium.

The 2*s* orbital of Hartree–Fock treatments of the neon atom provides an example of the difficulty of obtaining accurate solutions to the eigenvalue equations near a node in the wavefunction. Figure 2 shows the 2*s* orbital's local eigenvalue for three basis sets each of which has optimized exponents: minimum[5], double-zeta[4], and extended[6] (6*s*, 4*p*). Each of the bases shows wild variation in the local 2*s* eigenvalue out to the node in the 2*s* orbital (at 0.3 bohr). Beyond that radius, the extended basis is clearly superior to the smaller sets. The root mean square deviation of the local eigenvalue for the 2*s* orbital in neon is dominated by the region near the node. Consequently, the values for it seem large. The extended basis set gives by far the best $\Delta = 1.86$; the minimum basis result is 2.44, and the

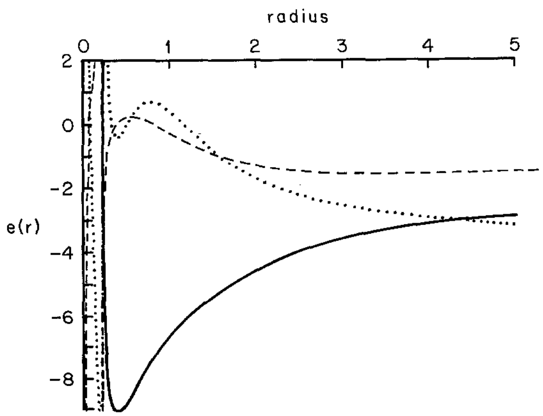

Fig. 2. The local eigenvalue (in atomic units) for the neon 2*s* orbital is shown for three basis sets: minimum (· · · ·), double-zeta (——), and extended (- - -)

double-zeta value is 5.52. The neon 1*s* orbital is, of course, nodeless, and its local eigenvalue is much better behaved with a $\Delta = 0.778$ for the extended basis set.

It is proposed that the spatial variation of the local orbital eigenvalues is a fairly easy test of the relative quality of a basis set in any electronic structure calculation. The Hartree–Fock example worked out here is readily generalizable to unrestricted Hartree–Fock, valence-bond, or other methods, thereby generating a basis set test that is specific to the type of wavefunction under consideration. Because of the erratic behavior near orbital nodes, it seems best not to rely on the root mean square deviation numbers, but to make a more qualitative comparison of plots of the spatial variation of the local eigenvalues.

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