

COMMENT

Reply to “Comment on ‘Depurated Inversion Method for Orbital-Specific Exchange Potentials’”

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The asymptotic behavior of Hartree-Fock orbitals has been studied by many authors since Handy, Marron and Silverstone (HMS)^[1] demonstrated that at large distances r , the radial parts of the Hartree-Fock orbitals u_{nl} are controlled by the energy of the highest occupied molecular orbital $\epsilon_{\text{HOMO}}^{\text{HF}}$

$$\lim_{r \rightarrow \infty} u_{nl}^{\text{HF}}(r) = \exp\left(\sqrt{-2\epsilon_{\text{HOMO}}^{\text{HF}}}r\right). \quad (1)$$

This behavior was confirmed by additional derivations, for example, by the work of Handler, Smith and Silverstone,^[2] and Ishida and Ohno.^[3] As pointed out by Cinal in his comment, the correct asymptotic form for the corresponding *exact* Hartree-Fock potentials V_{nl}^{HF} is^[4]

$$\lim_{r \rightarrow \infty} V_{nl}^{\text{HF}}(r) = -\left(\epsilon_{\text{HOMO}}^{\text{HF}} - \epsilon_{nl}^{\text{HF}}\right) + \frac{q_{nl}}{r}, \quad (2)$$

where $\epsilon_{nl}^{\text{HF}}$ are the HF orbital energies, and q_{nl} is usually different from -1 .

In our article,^[5] we presented a numerical method allowing us to obtain orbital-specific effective potentials (the Depurated Inversion Method - DIM). The method relies on the substitution of *any* orbital and energy into a Kohn-Sham-like equation. Through an inversion procedure, the corresponding effective potentials were obtained. After careful optimization of the charges, the poles were eliminated, and appropriate boundary conditions were set (*depuration*). The main application of these potentials is aimed at the simple generation of the wavefunctions of the particles interacting in dynamical processes. Specifically, to calculate the transition probabilities, a potential is required for the representation of the continuum states.^[6]

We assumed for all the potentials a Coulombic-type shape

$$V_{nl}^{\text{DIM}} = -\frac{Z_{nl}^{\text{DIM}}}{r}, \quad (3)$$

constraining the charges to behave as

$$Z_{nl}^{\text{DIM}}(r) \rightarrow \begin{cases} Z_N & \text{for } r \rightarrow 0 \\ 1 & \text{for } r \rightarrow \infty, \end{cases} \quad (4)$$

where Z_N is the nuclear charge. This condition at large distances is considered as the *exact* asymptotic behavior of the exchange-energy density in the seminal work of Becke.^[7]

The solutions to this potential do not follow the correct “Hartree-Fock” behavior. In place, they behave with the form called by Casida and Chong as a “Hartree-like” behavior^[8]

$$\lim_{r \rightarrow \infty} u_{nl}^{\text{DIM}}(r) = \exp\left(\sqrt{-2\epsilon_{nl}^{\text{HF}}} r\right) \quad (5)$$

(the term Hartree-like may be misleading since $\epsilon_{nl}^{\text{HF}}$ is the correct HF orbital energy, which includes the exchange).

In the following, we explain the reasons to sustain that for our undertaking, this is the correct behavior to assume.

1. First of all, we want to clearly state that the asymptotic form for the HF orbitals (1) and for the exact HF potential (2) have been rigorously demonstrated by the theory, and we never cast doubt upon that. However, many authors have questioned their relevance and being unsure whether this behavior “has physical significance or is just an artifact of the HF method” (quoted from the foundational paper (HMS) ^[1]). Handler and Smith recognized these concerns but stated that “the Hartree–Fock model is well defined and the matter of its behavior is of intrinsic interest for the study of its structure”.^[2] Weber and Parr went much further into this “moot question”. They propose to limit the exchange effects to a finite “sphere of influence” of the electrons, assuming that “one may think of an electron which is removed from an atom as somehow distinguishable by the fact of separation. This electron in some sense sees the ion as just a classical positive charge if the separation distance is large enough, and, therefore, in this context, exchange effects may be neglected”.^[9]
2. The correct long-range behavior of the HF orbitals appears at very long distances. It is possible to study the asymptotic behavior in detail by analyzing the logarithmic derivative of the wavefunctions. We define

$$L_{nl}(r) \equiv r \frac{d \log u_{nl}}{dr}, \quad (6)$$

which behaves linearly for the exponentially decaying u_{nl} functions. As an illustrative example, we calculated the HF wavefunctions corresponding to the ground state orbitals of Na, numerically, by using the HF computational code by C. F. Fischer,^[10] and the NRHF code by W. Johnson.^[11] The u_{1s} (solid line) and the HOMO u_{3s} (dashed line) orbitals are plotted in the lower part of Figure 1. The modified logarithmic derivatives L_{nl} are given in the upper part of this figure. The long- r behavior of $L_{nl}(r)$ agrees with the expected HOMO slope, as indicated by Cinal's comment; the curves $L_{1s}(r)$ and $L_{3s}(r)$ are indistinguishable beyond $r = 10$ a.u. Additionally, the Hartree-like behavior is also attained for the u_{1s} , slightly beyond the turning point (for $0.2 < r < 1$ a.u.) (dotted line). Therefore, as in many other examples studied, we found that the physically important large- r part of the wavefunction is dictated by the “Hartree-like” behavior, rather than the exact “Hartree Fock” behavior. This is perhaps the reason why Weber, Handy and Parr ^[12] suggested to consider the long-range behavior (5) as desirable, producing more accurate results than those obtained by the formal HF theory. By inspecting the experimental ($e, 2e$) electron spectroscopy, Casida and Chong ^[8] also arrived at the same conclusions.

3. The Hartree-Fock theory is based on the variational principle, and the long-range decaying behavior of the wavefunctions has little effect on the energy values. However, the implications of the assumption of the exact exchange potential have devastating effects in any computational procedure involving inversion of the wavefunctions (like, for example, our DIM method). As seen in the inset of the lower part of Figure 1, the

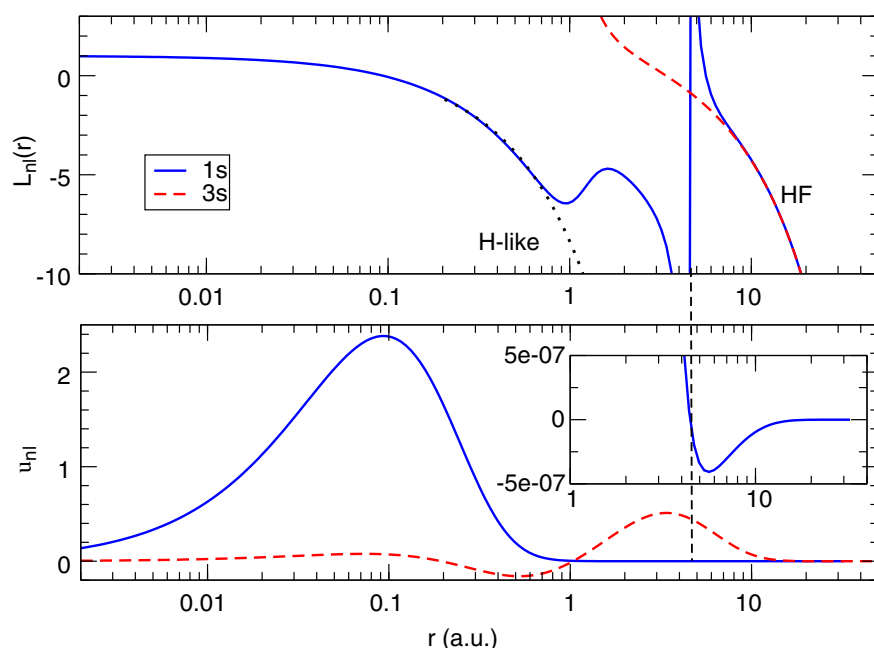


FIGURE 1 (upper) Modified logarithmic derivative $L_{1s}(r)$ for Na. Dashed line: $L_{3s}(r)$ (Hartree–Fock asymptotic behavior). Dotted line: Hartree-like asymptotic behavior. (lower) Hartree–Fock orbitals u_{1s} and u_{3s} for the ground state of Na. Inset: 1 s spurious node at $r = 4.4$ a.u.

u_{1s} orbital presents an unphysical spurious node at $r = 4.4$ a.u. The existence of spurious nodes in HF wavefunctions is not caused by the numerical scheme, but it is inherent to the method. Weber *et al.* conjectured that all signs of spurious nodes have disappeared when the "Hartree-like" behavior (5) is assumed, rather than the usual HF limit (1).^[12] As a general rule, the spurious nodes appear at very long distances, where the wavefunction amplitudes are negligible. Thus, their existence has no practical consequences, and they can, and should, be ignored in any general HF calculation. This is not true as far as the inversion procedure is concerned. As seen in the figure, the logarithmic derivative is meaningless over a wide range (in u_{1s} , for $1.2 < r < 8$). We do not see the point of why to make an effort to adopt the correct HF asymptotic behavior to reproduce the wavefunctions correctly over a region riddled by unphysical nodes.

- The DIM method has been designed to fulfill a useful task: the computation of collisional processes. From this point of view, the exact HF potentials are impractical; they have poles at each node of the wavefunctions, they can not be diagonalizable, their corresponding charges diverge and are deeply spoiled by spurious nodes. Assumption (3) provides the most accurate way to approximate the effective potentials with a simple numerical expression since their behavior is mostly Coulombian. In place of adjusting a diverging potential - which covers a vast range of values -, the fitting is performed over the charge, constituting a smooth and bounded function. As a net result, the DIM effective potentials vary smoothly, yielding a charge which interpolates between an attractive nuclear charge Z_N near the origin and an effective charge +1 in the asymptotic region. The potentials have a simple analytic form, and their diagonalized solutions reproduce the original wavefunctions with a very high accuracy and quality. As far as our needs, the DIM scheme accomplishes our targets at large.
- At this stage, it is important to stress out that the mere existence of a local Hartree-Fock potential is questionable. For instance, Amusia *et al.*^[13] demonstrated that the HF density is not v -representative, that is, it cannot be obtained as the ground state density of non-interacting electrons in a local potential. However, we successfully obtained many V_{nl}^{DIM} effective potentials able to reproduce with excellent accuracy the HF orbital wavefunctions, their total and exchange energies, and the mean orbital values, for a variety of atoms and ions, and for different configurations. As an example, our results in^[5] show that the DIM potentials reproduce the HF energies with several significant figures, and the total exchange energies with values very close to those given by Becke.^[7] In the worse case, the error is about 0.04%.

In conclusion, we claim that the asymptotic behavior (4) assumed for the DIM effective charges is appropriate.

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