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**ONE-BODY POTENTIAL THEORY OF MOLECULES  
AND SOLIDS MODIFIED SEMIEMPIRICALLY  
FOR ELECTRON CORRELATION**

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**Abstract**

The study of Cordero, March and Alonso (CMA) for four spherical atoms, *Be, Ne, Mg* and *Ar*, semiempirically fine-tunes the Hartree-Fock (HF) ground-state electron density by inserting the experimentally determined ionization potentials. The present Letter, first of all, relates this approach to the very recent work of Bartlett ‘towards an exact correlated orbital theory for electrons’. Both methods relax the requirement of standard DFT that a one-body potential shall generate the exact ground-state density, though both work with high quality approximations. Unlike DFT, the CMA theory uses a modified HF non-local potential. It is finally stressed that this potential generates also an idempotent Dirac density matrix. The CMA approach is thereby demonstrated to relate, albeit approximately, to the DFT exchange-correlation potential.

**Key words:** Correlated orbitals, Non-local potential, Dirac density matrix

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Some six decades ago, March and Murray [1, 2], by means of infinite order perturbation theory, set up a one-body potential theory suitable for treating molecules and defective solids. Their approach adopted a local potential  $V(\mathbf{r})$ , already considered by Slater [3] as a simplification of the Hartree-Fock method, the latter involving essentially a non-local one-body potential due to the presence of the Fock operator [4]. Subsequently, Slater's work on the one-body potential  $V(\mathbf{r})$  was formally completed by Kohn and Sham [5]. These authors demonstrated that the potential  $V(\mathbf{r})$  had an exchange-correlation component  $V_{xc}(\mathbf{r})$  which must be added to the Hartree potential:

$$V(\mathbf{r}) = V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) . \quad (1)$$

Unfortunately the result in [5], namely

$$V_{xc}(\mathbf{r}) = \frac{\delta}{\delta n(\mathbf{r})} E_{xc}[n] \quad (2)$$

involves the as yet unknown energy functional  $E_{xc}[n]$ , where  $n$  is the electron density.

While major progress in quantum chemistry has resulted from a number of proposed approximate energy functionals  $E_{xc}$  [6], there is presently no systematic procedure to ensure that 'refinements' of such available functionals will converge to the exact ground-state energy  $E$ . And indeed, while the Slater-Kohn-Sham (SKS) form of density functional theory (DFT below, see, e.g. Parr and Yang [7]) is a variationally based method for Fermions, Amovilli et al. [6] have recently shown in this Journal that three out of four currently popular forms of  $E_{xc}[n]$  lead to ground-state energies below the exact  $E$  for some of the trial test cases for which  $E$  is known from correlated wave function theory or quantum Monte Carlo (QMC) simulations. This, of course, is a deeply serious matter for it means that some of the widely used forms of  $E_{xc}$  and hence  $V_{xc}$  in eqn.(2) cannot have any underlying antisymmetric many-electron wave function.

Subsequent to the work of [6] Bartlett has recently written a frontiers article [8] entitled 'towards an exact correlated orbital theory for electrons'. In this review, Bartlett also stresses that DFT methods 'are fraught with difficulty', and he notes in specific terms numerous errors in present functionals, in addition to the possible violation of the variational principle by some choices of  $E_{xc}[n]$  which are currently widely used in quantum chemistry, as earlier demonstrated in [6].

However, our aim in the present Letter is to compare and contrast the proposal of Bartlett on a correlated orbital theory, with the earlier study of Cordero, March and Alonso [9]. This is especially prompted by Bartlett's writing, and we quote again here, 'our one-particle theory will look almost like Hartree-Fock theory ...'. That description will be shown to apply quite precisely also to [9], with, however, the, of course major, difference that Cordero et al. invoke semiempirical 'fine-tuning' of the ground-state Hartree-Fock (HF) density. However, given that Cordero et al. impose, in a spherical atom like *Be* or *Ne*, the experimental ionization potential  $I$  (as they stress, to be corrected by a method they outline for usually small relativistic effects when necessary), their approach already constitutes one example of a (now approximate, of course)

correlated orbital theory for electrons. Briefly, the idea underlying [9] is to ‘fine tune’ the already highly accurate  $n(\mathbf{r})$  of HF theory [10] to remove the difference between the ionization potential of Koopmans, denoted there by  $I_K$ , and the exact (non-relativistic) ionization potential  $I$ .

Put precisely, following [11], the asymptotic large  $r$  limit of the ground-state electron density of a non-relativistic spherical atom is given in atomic units by

$$n(r)|_{r \rightarrow \infty} = Ar^\gamma \exp(-2\sqrt{2I}r) . \quad (3)$$

In HF theory with its non-local potential, all the individual orbitals building up the density in eqn.(3) fall off in the same exponential manner governed by  $I_K$  in marked contrast to the case of a local potential  $V(r)$ .

The achievement of Cordero et al. is to modify HF theory to retain the Kato cusp at the nucleus (see eqn.(5) below) but to ensure the correct asymptotic form (3) by building in the measured  $I$ , as mentioned already, into eqn.(3).

The semiempirical correlated orbital theory of CMA, in the language of RJB, consists of the following, published so far for the spherical atoms  $Be, Ne, Mg$  and  $Ar$  ground-states:

- (i) Solve the self-consistent field (SCF) HF equations [9] numerically. However, this solution is now, because of semiempirical inclusion of correlation, not for the integral atomic number  $Z$  (i.e. 4 for  $Be$ : 10 for  $Ne$  etc.), but for a fractional value,  $Z'$  say, near to  $Z$ . The value of  $Z'$  is fixed precisely by appeal to the experimentally measured ionization potential  $I$  (corrected, when necessary, for usually small relativistic effects: see [9]). The resulting normalized density  $n(r, Z')$  thereby obtained from occupied normalized HF orbitals  $\psi_i(r, Z')$  for neutral atoms with  $N$  electrons, i.e.  $n(r, Z')$  has  $N = Z$ , not  $Z'$ . This density  $n(r, Z')$ , before final modification, describes either fractional cations or anions, but not neutral atoms.
- (ii) This density is then scaled to a final density

$$n_\lambda(r) = \lambda^3 n(\lambda r, Z') \quad (4)$$

where  $\lambda$  is to be determined to satisfy the Kato cusp condition [12]. For atoms this reads

$$\left. \frac{\partial n(r)}{\partial r} \right|_{r=0} = -\frac{2Z}{a_0} n(r=0) : a_0 = \frac{\hbar^2}{me^2} . \quad (5)$$

By detailed comparison with available QMC simulations, it turns out for the four atoms cited above that the ground-state densities thereby obtained are of QMC quality. The fact that this semiempirical fine-tuned HF density: to be determined by steps (i) and (ii) explained above, is an excellent approximation to the true ground-state density  $n(r)$ , has its origins in the work of Moller and Plesset, some  $6\frac{1}{2}$  decades ago [10], who by HF perturbation theory proved that the HF ground-state density was correct to second-order in the difference between the Fock operator and the exact non-relativistic Hamiltonian.

We stress again that, as with the recent RJB proposal [8], the SKS requirement of an exact ground-state density [7] is relaxed slightly, in the CMA correlated orbital theory, by means of adapting the one-body HF potential which is, as mentioned above, intrinsically non-local. Returning for a moment to the RJB method [8], there it is explicitly concluded that ‘our one-particle theory will look almost like Hartree-Fock theory etc.’, making clear the similarities between the CMA semiempirical theory and the method of RJB. A second important similarity is the insistence in both methods that the ionization potential  $I$  is exact: as explained above this is put in ‘by hand’ in the CMA method by making use of the experimentally measured value. RJB in this latter respect goes further, at least in principle, in insisting that his approach guarantees a correct one-particle energy spectrum, but with an approximate density paralleling that in the CMA theory.

Returning to semiempirical approaches, we want to emphasize here that the ultimate aim of these would be to utilize the measured ground-state electron density  $n(\mathbf{r})$  for molecules and solids. As a specific example we cite the work of Howard et al. [13] on a crystal of formamide. Following an approach now referred to as ‘quantum crystallography’ by workers in the field; notable names being J. Karle and L. Massa, one sets up an approximate, but nevertheless idempotent, density matrix of Dirac [14] single-particle(s) form

$$\gamma_s(\mathbf{r}, \mathbf{r}') = \sum_{\text{occupied } i} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}') \quad (6)$$

where the  $\psi_i(\mathbf{r})$  denote orthonormal orbitals. The property of idempotency, plus the fact that eqn.(6) is such that  $\gamma_s(\mathbf{r}, \mathbf{r}) = n(\mathbf{r})$ , the measured ground-state density from, say, X-ray diffraction experiments, are the important characteristics of eqn.(6).

But, in practice, the approach of the crystallographers is less directly related to correlated orbital theory than eqn.(6) would suggest. Therefore, below, we shall (i) emphasize the precise procedure adapted in current applications of quantum crystallography and (ii) stress that approximations to  $\gamma_s(\mathbf{r}, \mathbf{r}')$  in eqn.(6) can lead us to link correlated orbital theory, as in the CMA approach, to current DFT theory.

Starting with step (i) above, eqn.(6) is approximated by (compare Holas and March [15]) an expansion in a finite basis of  $K$  orbitals  $\chi_i(\mathbf{r})$  as

$$\gamma_s(\mathbf{r}, \mathbf{r}') = \sum_{ij}^K P_{ij} \chi_i(\mathbf{r})\chi_j(\mathbf{r}') . \quad (7)$$

The orbitals  $\chi_i$  may be chosen as real, which is always possible in the absence of a magnetic field. The symmetric matrix  $P_{ij}$  entering eqn.(7) is a compact representation of the parameters used in quantum crystallography to fit the measured Bragg reflection data, say on the solid in question.

We take as an immediate example the work of Howard et al. [13] on formamide, already referred to. An X-ray experiment on this molecule in its crystalline geometry had earlier been

carried out by Stevens [16]. The analysis reported in [13] leads to an idempotent matrix which has the experimentally determined ground-state density  $n(\mathbf{r})$  as its diagonal element  $\gamma_s(\mathbf{r}, \mathbf{r})$ .

But this now takes us back to correlated orbital theories distinguished by the use of local potentials, as in the SKS method, and the HF-like non-local potential of the CMA approach. For the former case, the idempotent Dirac matrix  $\gamma_s(\mathbf{r}, \mathbf{r}')$  defined via eqn.(6), satisfies the equation of motion [17]

$$\nabla_{\mathbf{r}}^2 \gamma_s - \nabla_{\mathbf{r}'}^2 \gamma_s = \frac{2m}{\hbar^2} [V(\mathbf{r}) - V(\mathbf{r}')] \gamma_s \quad (8)$$

where  $V(\mathbf{r})$  is given in eqn.(1). Idempotency must, of course, be imposed on the physical solution of eqn.(8). But immediately we encounter the difficulties spelt out above concerning the exchange-correlation potential  $V_{xc}(\mathbf{r})$  in Eq. (1).

Thus, Holas and March [15] have advocated an extension of the quantum crystallographic approach discussed above by applying a potential-locality constraint to the approach of Howard et al. [13]. This specific constraint has not yet, to the present writer's knowledge, been applied to the experimental data on formamide, but the way to do this is set out very specifically in section III of Holas and March [15].

In the absence of this necessary data on a semiempirical Dirac density matrix  $\gamma_s(\mathbf{r}, \mathbf{r}')$  constructed from experiment X-ray intensities, which we regard as the 'ultimate' semiempirical approach, let us approach our conclusion by returning to the correlated orbital approach of CMA, in which only the experimental ionization potential is introduced semiempirically. The CMA approach has been subsequently generalized off the diagonal by Amovilli, March and Talmán [18], to form a Dirac density matrix  $\gamma_s(\mathbf{r}, \mathbf{r}')$  with the CMA density as its diagonal element  $\gamma_s(\mathbf{r}, \mathbf{r})$ . We must reiterate that this  $\gamma_s$  does not satisfy eqn.(8), since the Amovilli et al.  $\gamma_s$  is generated by a HF-like non-local potential. Nevertheless, there is a way, set out below, in which this 'non-locally' generated  $\gamma_s$  can be used to make intimate contact with current DFT [7].

The essence of the approach proposed below to connect, albeit approximately, the CMA correlated orbital theory with current DFT is to utilize the differential virial theorem derived by Holas and March [19]. Essential input is then the kinetic energy tensor  $t_{ij}$ , constructed from the Dirac density matrix  $\gamma_s(\mathbf{r}, \mathbf{r}')$  as (in atomic units)

$$t_{ij} = \frac{1}{4} \left[ \left( \frac{\partial^2}{\partial r_i \partial r_j'} + \frac{\partial^2}{\partial r_j \partial r_i'} \right) \gamma_s(\mathbf{r}, \mathbf{r}') \right]_{\mathbf{r}'=\mathbf{r}} \quad (9)$$

which leads to the force  $\mathbf{F}_K$  given by its components  $(F_K)_i$  as

$$(F_K)_i = \frac{2}{n(r)} \sum_{j=1}^3 \frac{\partial t_{ij}}{\partial r_j} \quad (10)$$

Then in eqn.(13) of Amovilli and March [20] the desired exchange-correlation potential in eqn.(1) above is given by

$$\begin{aligned}
V_{xc}(\mathbf{r}) = & -V_{es}(\mathbf{r}) + \frac{1}{16\pi} \int \frac{[\nabla n \cdot \nabla \nabla^2 n]}{n^2(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|}(\mathbf{r}')d\mathbf{r}' \\
& - \frac{1}{16\pi} \int \frac{\nabla^4 n(\mathbf{r}')}{n(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' + \frac{1}{4\pi} \int \frac{\nabla \cdot \mathbf{F}_K(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' .
\end{aligned} \tag{11}$$

In eqn.(11)  $V_{es}(\mathbf{r})$  is the electrostatic potential, while, of course, to obtain  $V_{xc}(\mathbf{r})$  exactly we need in eqn.(11) the exact ground-state density  $n(\mathbf{r})$  for, say, the molecule or cluster under investigation, plus the force  $\mathbf{F}_K(\mathbf{r})$  determined by the Dirac idempotent matrix  $\gamma_s(\mathbf{r}, \mathbf{r}')$  through eqns.(10) and (9).

One use of the CMA correlated orbital theory, which is a major proposal of the present Letter, is to now use instead of the exact  $n(\mathbf{r})$  entering eqn.(11) the CMA semiempirical fine-tuned HF density. The second approximation is to note that since  $\mathbf{F}_K(\mathbf{r})$  appears inside a volume integration in the final term in eqn.(11), we substitute for the idempotent Dirac matrix  $\gamma_s(\mathbf{r}, \mathbf{r}')$ , which should be generated from the exact local one-body potential  $V(\mathbf{r})$  in eqn.(1) via eqn.(8), the off-diagonal idempotent matrix given by Amovilli, March and Talman [18]. Of course, this has a QMC accuracy on the diagonal, but off the diagonal it is generated by a non-local HF-like potential [18, 9]. It would seem of considerable interest for the many-electron theory of molecules and solids if one can finally pull together correlated orbital theories such as CMA or RJB with current formulations of DFT, by means of Eqs. (9) to (11) above.

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