

# Combination of many-body and density-functional theories

Dimitri N. Laikov\*

*Department of Physics, AlbaNova University Center,  
Stockholm University, SE-10691 Stockholm, Sweden*

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## Abstract

A framework for developing new approximate electronic structure methods is presented, in which the correlation energy of a many-electron system in the ground state is computed as in the single-reference second-order many-body perturbation theory but with the reference one-body Hamiltonian modified by additional (generally non-local) potentials which are universal functionals of the Hartree-Fock density. The existence of such functionals that reproduce the exact correlation energy justifies the search for approximate models which may overcome some important deficiencies of the traditional density-functional methods and also perform better than the usual low-order wavefunction methods.

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\*Electronic address: laikov@physto.se

## I. INTRODUCTION

The Hohenberg-Kohn theorems [1] have provided a formal justification for the development of a number of approximate density functionals for electronic structure calculations within the Kohn-Sham scheme [2]. Such density-functional methods are now widely used in theoretical chemistry for computing ground state properties of molecules due to their low cost and scalability. Nevertheless, there is still a number of deficiencies that the traditional approximate functionals cannot overcome. Self-interaction error [3] is one such example, another important problem is the inability to describe the dispersion (van der Waals) interaction [4]. On the other hand, the simplest correlated wavefunction method – the Møller-Plesset second-order (MP2) many-body perturbation theory [5] – does not suffer from these deficiencies, its cost, though higher, is still acceptable for many interesting applications. There are cases, however, where this simple approximation shows its weakness – for strongly-correlated systems the correlation energy can be significantly overestimated, another difficulty appears when the underlying Hartree-Fock reference experiences an artificial spin- or symmetry-breaking.

In this work we propose a framework for developing new approximated methods of electronic structure calculations which combine the strengths of both the low-order many-body perturbation theory and the local density functional approximations.

## II. THEORY

Starting from the fact that the exact total energy of a many-electron system in the ground state is a functional of the Hartree-Fock density [6], we propose here a special form of the correlation energy functional for which simple approximate models may be developed.

The single-determinant wavefunction  $\Phi$  of the Hartree-Fock theory assumed normalized

$$\langle \Phi | \Phi \rangle = 1 \tag{1}$$

makes the expectation value of the energy

$$E_0 = \langle \Phi | \hat{H} | \Phi \rangle \tag{2}$$

stationary, which is equivalent to the conditions

$$\langle \Phi_i^a | \hat{H} | \Phi \rangle = 0, \tag{3}$$

where singly-substituted determinants  $\Phi_i^a$  are introduced. The indices  $i, j, k, \dots$  ( $a, b, c, \dots$ ) label the occupied (virtual) one-electron wavefunctions, whereas  $\kappa, \lambda, \mu, \nu$  will refer to any of them.

In terms of one- and two-electron integrals

$$H_\mu^\nu = \int \phi_\mu(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v(\mathbf{r})\right) \phi_\nu(\mathbf{r}) d^3\mathbf{r}, \quad (4)$$

$$R_{\kappa\mu}^{\lambda\nu} = \bar{R}_{\kappa\mu}^{\lambda\nu} - \bar{R}_{\kappa\mu}^{\nu\lambda}, \quad (5)$$

$$\bar{R}_{\kappa\mu}^{\lambda\nu} = \int \phi_\kappa(\mathbf{r})\phi_\mu(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1}\phi_\lambda(\mathbf{r})\phi_\nu(\mathbf{r}') d^3\mathbf{r} d^3\mathbf{r}', \quad (6)$$

where the wavefunctions  $\phi_\kappa(\mathbf{r})$  are assumed to be real and their spin dependence is not shown explicitly for simplicity, the energy (2) and the conditions (3) take the form

$$E_0 = H_i^i + \frac{1}{2}R_{ij}^{ij}, \quad (7)$$

$$F_i^a = 0, \quad (8)$$

with the Fock matrix defined by

$$F_\mu^\nu = H_\mu^\nu + R_{\mu i}^{\nu i}. \quad (9)$$

The summation over all repeated indices is assumed throughout.

We now introduce a first-order correlated wavefunction  $\Psi_1$  as a linear combination of all doubly substituted determinants

$$\Psi_1 = \frac{1}{4}\tau_{ij}^{ab}\Phi_{ij}^{ab}, \quad (10)$$

from which the (exact) correlation energy will be computed as

$$E_c = \langle \Psi_1 | \hat{H} | \Phi \rangle \quad (11)$$

or in terms of two-electron integrals

$$E_c = \frac{1}{4}\tau_{ij}^{ab}R_{ij}^{ab}. \quad (12)$$

The coefficients  $\tau_{ij}^{ab}$  are determined by linear equations

$$f_c^a\tau_{ij}^{cb} + f_c^b\tau_{ij}^{ac} - f_i^k\tau_{kj}^{ab} - f_j^k\tau_{ik}^{ab} + R_{ij}^{ab} = 0 \quad (13)$$

which are formally derived from many-body perturbation theory with the one-electron matrix elements of the zeroth-order Hamiltonian in the form

$$f_i^j = F_i^j + u_i^j, \quad (14)$$

$$f_a^b = F_a^b + u_a^b, \quad (15)$$

$$u_i^j = \int \phi_i(\mathbf{r}) u_o(\mathbf{r}; [\rho_0]) \phi_j(\mathbf{r}) d^3\mathbf{r}, \quad (16)$$

$$u_a^b = \int \phi_a(\mathbf{r}) u_v(\mathbf{r}; [\rho_0]) \phi_b(\mathbf{r}) d^3\mathbf{r}. \quad (17)$$

The two different ‘‘correction potentials’’  $u_o$  and  $u_v$  to be added to the one-electron Fock operator are universal functionals of the Hartree-Fock density

$$\rho_0(\mathbf{r}) = \phi_i(\mathbf{r})\phi_i(\mathbf{r}) \quad (18)$$

and have the property that the resulting correlation energy (11) is equal to the exact one. It is obvious that the correction potentials thus defined are not unique. The simplest form would be a constant shift (independent of  $\mathbf{r}$ ) for either all occupied or all virtual energy levels:  $u_o(\mathbf{r}) = u[\rho_0]$ ,  $u_v = 0$  or vice versa, but in that case the density functional  $u[\rho_0]$  should be highly non-local and very hard to model without violating the size-consistency of an approximate method. One would be interested in the models where these potentials were local in nature.

For the full-CI wavefunction of the form

$$\Psi_{\text{CI}} = \Phi + T_i^a \Phi_i^a + \frac{1}{4} T_{ij}^{ab} \Phi_{ij}^{ab} + \frac{1}{36} T_{ijk}^{abc} \Phi_{ijk}^{abc} + \dots \quad (19)$$

the correlation energy can be expressed as (12) in terms of the doubles coefficients  $T_{ij}^{ab}$  alone, so it would be natural to require the equations (13) to generate the values  $\tau_{ij}^{ab}$  which approximate  $T_{ij}^{ab}$  in (19). Having only  $n_o(n_o + 1)/2 + n_v(n_v + 1)/2 - 1$  matrix elements  $u_i^j$  and  $u_a^b$  as parameters ( $n_o$  and  $n_v$  are the dimensions of the occupied and virtual subspaces, the latter can be in principle infinite) it is not possible, in general, to reproduce all  $n_o(n_o - 1)n_v(n_v - 1)/4$  nontrivial values of  $T_{ij}^{ab}$ . The differences between the reduced one-electron quantities

$$Q_i^j = \tau_{ik}^{ab} \tau_{jk}^{ab} - T_{ik}^{ab} T_{jk}^{ab}, \quad (20)$$

$$Q_a^b = \tau_{ij}^{ac} \tau_{ij}^{bc} - T_{ij}^{ac} T_{ij}^{bc} \quad (21)$$

can be brought to zero by an appropriate choice of  $u_i^j$  and  $u_a^b$  in (13), in that case, however, the correlation energy (11) may differ from the exact one. The minimization of either

$$q = Q_i^j Q_i^j + Q_a^b Q_a^b \quad (22)$$

or

$$q = Q_i^j \bar{R}_{ik}^{jl} Q_k^l + Q_a^b \bar{R}_{ac}^{bd} Q_c^d \quad (23)$$

with respect to  $u_i^j$  and  $u_a^b$  with the constraint of reproducing the full-CI correlation energy by (12) leads to the equations which uniquely define the correction potentials in either case. A more simple function

$$q = (\tau_{ij}^{ab} - T_{ij}^{ab}) ((F_c^a \delta_{bd} + F_d^b \delta_{ac}) \delta_{ik} \delta_{jl} - \delta_{ac} \delta_{bd} (F_i^k \delta_{jl} + F_j^l \delta_{ik})) (\tau_{kl}^{cd} - T_{kl}^{cd}) \quad (24)$$

can also be used as a measure of the deviation between the doubles coefficients.

The existence of such (not necessarily multiplicative) potentials  $u_o(\mathbf{r}; [\rho_0])$  and  $u_v(\mathbf{r}; [\rho_0])$  as functionals of the Hartree-Fock density follows from the fact that there is a one-to-one mapping between the external potential  $v(\mathbf{r})$  and the Hartree-Fock density  $\rho_0(\mathbf{r})$ , the relationship can be schematically described as  $\rho_0 \Rightarrow v \Rightarrow \Psi_{\text{CI}} \Rightarrow u_o, u_v$ .

In analogy to the traditional density-functional theory the development of approximate functionals of this new type can start from the consideration of the uniform electron gas as the simplest model system. A local density approximation of the form

$$u_o(\mathbf{r}) = u^{\text{ueg}}(\rho_0(\mathbf{r})) \alpha(\rho_0(\mathbf{r})), \quad (25)$$

$$u_v(\mathbf{r}) = u^{\text{ueg}}(\rho_0(\mathbf{r})) (1 + \alpha(\rho_0(\mathbf{r}))), \quad (26)$$

can be proposed, where the function  $u^{\text{ueg}}(\rho)$  is chosen as to reproduce, within this method, the exact correlation energy of the uniform electron gas, and the function  $\alpha(\rho)$  can be parametrized in some way, the simplest choices being the constants  $\alpha = 0$  or  $\alpha = -1$ .

### III. CONCLUSIONS

The new form of the correlation energy functional of the Hartree-Fock density proposed here is based on a physically meaningful description of the electron correlation using the two-particle equations (13). Approximate methods of this type should be able to describe the dispersion interaction in a natural way and should not contain self-interaction error. It remains to be seen if the simplest local density approximation (25) and (26) will show higher accuracy in molecular applications than the standard MP2 method. Such comparison will become possible as soon as the function  $u^{\text{ueg}}(\rho)$  will be available from numerical calculations of the uniform electron gas, which we are currently investigating. More sophisticated density-functional models of our corrections potentials  $u_o(\mathbf{r}; [\rho_0])$  and  $u_v(\mathbf{r}; [\rho_0])$  can also be

developed, an empirical parametrization [7] being the simplest choice.

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- [1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- [2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- [3] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- [4] W. Kohn, Y. Meir, and D. E. Makarov, Phys. Rev. Lett. **80**, 4153 (1998).
- [5] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
- [6] E. R. Davidson, Phys. Rev. A **42**, 2539 (1990).
- [7] A. D. Becke, J. Chem. Phys **107**, 8554 (1997).