Correlation forces in electron scattering from atoms and molecules: a density functional approach*

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Abstract

The behaviour of the short-range generalized response function in low-energy electron scattering from atoms (and molecules) is a very important component for the quantitative study of resonances and elastic scattering cross sections of electronic targets in the ground state, and for the prediction of inelastic processes involving all the available internal degrees of freedom of the multiparticle systems. In the present work new functional representations of such forces are devised, using short-range correlation energy formulae obtained for bound many-electron systems via different types of density functional theories. Comparison is made between the various expressions, as their likely effect on scattering observables is briefly discussed, in the case of elastic scattering from rare gas atoms.

INTRODUCTION

The scattering of low energy (1–50 eV) electrons from atoms and molecules is a complicated process involving several partial waves and the virtual excitation of many intermediate states (see, for example, ref. 1). In the forward-scattering region (θ < 50°) the interaction is largely dominated by the long-range dipole forces (when existing) between the incoming electron and the molecule. For large angles, however, the scattering is sensitive to the short-range features of the molecular dynamics, which

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*The present work is dedicated to the memory of Professor Charles A. Coulson, to honour the fortieth anniversary of the publication of his seminal book "Valence". One of us (FAG) had the great privilege of being a graduate student of his, and remembers very vividly how effectively the contents of that book were explained and commented on during the Professor's marvellous lectures.

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include the Coulomb forces, together with the exchange and correlation effects.

It is interesting to note that in the traditional description of chemical bonds and of the electronic foundations of chemical valence (see, for example, ref. 2) the above effects also play a crucial role in correctly depicting the way in which the bound electrons form the atomic aggregates. In the case of scattering processes, however, one is mainly concerned with introducing such many-body forces within the dynamical picture of an impinging electron experiencing multiple scattering from the bound electrons over the whole molecular volume and in the presence of the strong nuclear cusps. In other words, the effect on the electronic kinetic energy is averaged over the whole interaction space in which the various exit channels have been defined; the corresponding effects for the bound-state models in chemical bonds need to be carefully balanced within the more limited, square-integrable nature of the single-particle orbitals involved in the bond.

This essentially means that the study of the quantum processes occurring during the scattering of relatively slow electrons from atomic or molecular targets involves the setting up of a large (in principle, infinite) ensemble of coupled differential equations with integral terms describing bound–continuum exchange forces and with the more or less rigorous inclusion of the nuclear degrees of freedom [3].

The aim of the present paper is to describe a novel approach to the evaluation of some of the forces at play, i.e. that part of the full interaction which more explicitly involves the correlated motions of all \((N + 1)\) electrons in the system, where \(N\) is the number of bound electrons in the target atom or molecule.

The adiabatic polarization potential is defined to be the change in the total energy of the electron–target system caused by the distortion of the target’s charge distribution by the scattering electron. In the above definition the target orbitals can be fully relaxed in the presence of the projectile at a fixed position, whereby the kinetic energy of the latter can be disregarded [4]. This is predicated on the assumption that the target electrons respond adiabatically to the motion of the scattering electron, adjusting immediately to changes in the instantaneous position of the projectile. This approximation is valid for slow collisions but does not apply near the target, where the static exchange interaction becomes strongly attractive and the local velocity (in a classical sense [5]) of the scattering electron becomes comparable to that of the bound electrons. It is therefore mostly near the target that the response of the molecular electrons is not adiabatic, so the use of only its asymptotic form inevitably overestimates the true effects of polarization [6]. Thus, within the above picture one could tentatively identify three main "regions" where the correlation forces have to
be described with different methods, depending on the distance of the
scattering electron from the overall charge distribution (or rather from the
total centre of mass) of the target. In the outermost asymptotic region, the
second-order perturbation theory is valid and the correlation interaction
becomes the polarization potential with its familiar analytic form [7,8] from
the induction series

\[ V_{\text{Po}}^{A_1}(r,R) \approx \sum_{l=1}^{\infty} \frac{\alpha_l(R)}{2^{2l+1}r^{2l+2}} \]

where \( A_1 \) is labelling the target electronic state, \( R \) collectively describes
the nuclear coordinates (for a molecular target) and \( r \) is the position vector
of the scattering electron. Here \( \alpha_l \) is the multipole polarizability of the
target which, for the H atom, is given by [8]

\[ \alpha_l = \frac{(2l + 1)!(l + 2)}{2^{2l+1}l} \]

It is usually sufficient to stop at the first term in the eqn. (1), corresponding
to the dipole polarizability term

\[ V_{\text{Po}}^{d}(r,R) \approx \frac{\alpha_0(R)}{2r^4} - \frac{\alpha_2(R)}{2r^4} \mathbf{P}_2(\hat{r} \cdot \hat{R}) \]

where the spherical component \( \alpha_0 \) applies to atoms and the two components
together describe a diatomic molecular target.

For the second (intermediate) region the adiabatic approximation is still
valid, but contributions from terms of higher than second order in the
electron–electron interaction should be included. They could be either
repulsive or attractive, thus changing the gradient exhibited by the outer,
asymptotic potential.

Finally, the near-target region is badly described by eqn. (1), which
grossly overestimates polarization and correlation effects and incorrectly
diverges near the origin of the forces. Hence non-adiabatic corrections
must be taken into account and a different theoretical picture needs to be
put together. This is the subject of the present study.

The work is organized as follows. The next section (The correlation
forces) describes different approximations to the short-range correlation
energy derived from density functional models and uses them to extract
different non-adiabatic corrections for the asymptotic polarization poten-
tial of eqn. (1). The following section (Results and discussion) computes
numerically the functional derivatives of the previous energy expressions
to obtain the full correlation–polarization interaction between the scatter-
ing electron and the target electrons. Examples for the whole series of rare
gases are given and the results discussed in terms of their possible effects
on total elastic cross sections.
THE CORRELATION FORCES

Since the early days of quantum mechanics, several attempts have been made to reduce complicated, many-body problems to effective one-body problems. The most popular approaches have shown that a many-body system can be dealt with statistically as a one-body system by relating the local electron density \( \rho(r) \) to the total average potential \( V(r) \) felt by the electron in the many-body case. These approaches therefore produced the two mean-field equations known as Hartree–Fock–Slater (HFS) (see ref. 9) and Thomas–Fermi–Dirac (TFD) [10] equations. It was further thought that an alternative formulation based on a density theory instead of on a wavefunctional theory would avoid the full solution of the eigenvalue problem and aim instead at a global knowledge of the nature of the electronic ground state [11–13].

A more rigorous mathematical foundation of a density-based theory, known as the density functional theory (DFT) was established when Hohenberg an Kohn [14] provided a basic theorem stating that the ground state properties of an inhomogeneous many-body system can be expressed as a unique functional of its particle density. In the last two decades the DFT approach has therefore emerged as a powerful tool for the analysis of a large variety of atomic and molecular systems [15–17] and is beginning to appear in the areas of structure studies and scattering problems.

In scattering problems, in fact, the DFT can be used to deal with two basic difficulties in modelling the slow continuum-electron interaction with the target system: the bound-continuum non-local exchange terms required by the Pauli principle and the short-range correlation forces that include the non-adiabatic effects in addition to the asymptotic polarization forces. It is interesting to note at this point that the correct definition of short-range correlation forces, with their direct and exchange contributions, is still not entirely clear from the current literature [18,19]; it is undergoing a rather detailed analysis from the point of view of finding its correct short-range behaviour. In the next section (The CS short-range correlation formula) we summarize the meaning of such forces in the strong overlap region as they are employed by the traditional quantum chemical language and as they can be reformulated within a DFT approach. Such forces guide us in defining the behaviour of short-range correlation potentials between continuum electrons and the bound electrons of the target system. Their asymptotic form, however, can be recovered simply by including the known analytic form of the leading coefficients in the induction series of eqn. (1) and by smoothly connecting them with the local form of the short-range correlation potential from the density functional analysis.
The Colle–Salvetti (CS) short-range correlation formula

In the realm of correlation energy corrections to the total electronic energy of Born–Oppenheimer (B–O) molecular configurations, the earlier work of Wigner [20] was extended a few years ago [21–23] to obtain an approximate expression for the correlation energy (CE) in terms of one- and two-particle density matrices that could in turn be produced, if necessary, even by simple SCF computations. The general idea of the method was that of focussing on the short-range contribution to the CE, i.e. that part of the CE which derives from the electronic motion in those regions of electronic coordinate space where exchange and overlap effects indeed cause the breakdown of the asymptotic perturbative approaches [7]. The corresponding physical idea was that the main contribution to this short-range part of the CE comes from \( e^-\text{e}^- \) collisions at fairly high relative velocities, thus having effective cross sections related only to the local charge density of the system under study. Hence, the corresponding two-electron functional was derived with a procedure based only on equations relating first- and second-order density matrices via a particular choice for the Coulomb hole function [23]. In the following treatment we call the above derivation the Colle–Salvetti (CS) correlation energy, as obtained from a specific “ansatz” for the correlated wavefunction. The final, approximate expression was derived by considering, in fact, the correlated wavefunction for \( N \) electrons having the following form

\[
\psi(x_1, \ldots, x_N) = \phi^{HF}(x_1, \ldots, x_N) \prod_{i<j}^{N} \{1 - \phi(r_i, r_j)\} \tag{4}
\]

Here \( \phi^{HF} \) represents a reference, zeroth order Hartree–Fock (HF) wavefunction obtained either from a single-deter (SD) or a multiconfiguration (MC) description of the involved orbitals. The variable \( x \) denotes, as usual, both spatial and spin coordinates, while the short-range correlation function \( \phi \) was given by

\[
\phi(r_i, r_j) = e^{-\beta(R)^2} [1 - \Theta(R)(1 + \frac{1}{3})] \tag{5}
\]

with

\[
r = |r_i - r_j| \quad R = \frac{1}{3}(r_i + r_j) \tag{6}
\]

Following the early suggestions of Wigner and Seitz [24], the parameter \( \beta(R) \) was related to the excluded electron volume \( V_e \), i.e. to the spatial region in which \( \phi(r_i, r_j) \) is appreciably different from zero [4]

\[
V_e = 4\pi \int e^{-\beta r^2} r^2 \, dr = \frac{\pi^{3/2}}{\beta^{3/2}} = k\rho^{-1} \tag{7}
\]

where \( \rho \) is the total electron density and the constant \( k \) represents the
average number of electrons in $V_e$ [20]. Thus, one can further write

$$\beta = \frac{\pi^{1/2}}{6} \rho^{1/3} = q \rho^{1/3}$$  \hspace{1cm} (8)$$

where the constant $q$ needs now to be determined. If one makes the simple but reasonable approximation that the spinless second-order density matrix $P_2$ can be approximated by using the corresponding HF density matrix, $P_2^{\text{HF}}$ (see, for example, ref. 25)

$$P_2(r_1, r_2, r'_1, r'_2) = N(N - 1) \int \psi(x_1, x_2, x_3, \ldots x_N)$$

$$\cdot \psi^*(x'_1, x'_2, x'_3, \ldots x'_N) d\sigma_1 \ldots d\sigma_N dr_3 \ldots dr_N$$

$$\approx P_2^{\text{HF}}(r_1, r_2, r'_1, r'_2) \{1 - \phi(r_2, r_1)\} \{1 - \phi(r'_2, r'_1)\}$$  \hspace{1cm} (9)$$

and that the exact first-order density matrix is also given by its Hartree–Fock approximation

$$P_1(r_1, r'_1) = N \int \psi(x_1, x_2, \ldots x_N) \psi^*(x'_1, x_2, \ldots x_N)$$

$$\cdot d\sigma_1 \ldots d\sigma_N dr_2, \ldots dr_N \approx P_1^{\text{HF}}(r_1, r'_1)$$  \hspace{1cm} (10)$$

and further remembers that the total electronic energy can be written as

$$E_{\text{TOT}} = E_{\text{HF}} + E_{\text{corr}}$$

$$= \int \left[ h(r_1) P_1(r_1, r'_1) \right]_{r_1}^{r'_1} dr_1 + \frac{1}{2} \int \frac{1}{r_{12}} P_2(r_1 r_2, r_1, r_2) dr_1 dr_2$$  \hspace{1cm} (11)$$

with

$$h(r_1) = -\frac{1}{2} \nabla_1^2 - \sum_k \frac{1}{R_{K1}}$$  \hspace{1cm} (12)$$

Then the recursion relations between density matrices of successive orders allow one to write

$$\int P_2^{\text{HF}}(r_1, r_2, r'_1, r'_2) \{ \phi(r_1, r_2) \phi(r'_1, r'_2) - \phi(r_1, r_2) - \phi(r'_1, r'_2) \} dr_2 = 0$$  \hspace{1cm} (13)$$

By substituting this result in eqn. (11) one finally obtains an approximate expression for $E_{\text{corr}}$

$$E_{\text{corr}} \approx \frac{1}{2} \int \frac{1}{r_{12}} P_2^{\text{HF}}(r_1, r_2, r_1, r_2) \{ \phi^2(r_1, r_2) - 2\phi(r_1, r_2) \} dr_2 dr_1$$  \hspace{1cm} (14)$$

a formula which permits the calculation of the correlation energy starting from the knowledge of $P_2^{\text{HF}}$ at the points $r_1 = r'_1$ and $r_2 = r'_2$.

The condition expressed by eqn. (13) can be rewritten for $r_1 = r'_1$ and by
using the definition (eqn. (5)) of the correlation function
\[ \int P_2^H(F(R_1, r_2) \Theta(R) \left(1 + \frac{r}{2} \right) e^{-\beta \gamma^2} dr_2 
+ 2 \int P_2^H(F(R_1, r_2) \Theta(R) \left(1 + \frac{r}{2} \right) e^{-\beta \gamma^2} [1 - e^{-\beta \gamma^2}] dr_2 
- \int P_2^H(F(R_1, r_2) e^{-\beta \gamma^2} [2 - e^{-\beta \gamma^2}] dr_2 = 0 \]
(15)

one can obtain the limiting values of \( \Theta(R) \) [21]
\[ \Theta(R) \propto \sqrt{\pi} \beta \]
(16a)
\[ \Theta(R) \propto \frac{1}{\sqrt{\pi} \beta} \]
(16b)

which can be combined into an approximate expression for the correlation function
\[ \Theta(R) \approx \frac{\sqrt{\pi} \beta}{1 + \sqrt{\pi} \beta} \]
(17)

In order to reproduce from eqn. (14) the correct value of \( E_{\text{corr}} \) for the He atom, the parameter \( q \) in eqn. (8) was fixed at the value of 2.29. Furthermore, by making a second order expansion of \( P_2^H \) and using eqns. (5), (8) and (17), the CS approach of eqn. (4) produces an approximate relationship between \( E_{\text{corr}} \) and the one- and two-particle HF density matrices [21,22]
\[ E_{\text{corr}} = -2\pi \int P_2^H(R) H(\beta, \omega) \frac{1}{\beta^3} dR \]
(18)

where the explicit expression of \( H(\beta, \omega) \) and of \( \omega \) have been given previously [23]. The above expression can also be written as
\[ E_{\text{corr}} = -\frac{\pi}{q^2} \int \rho(R) G(\beta, Z) dR \]
(19)

where
\[ Z = \left( \frac{\nabla_r^2 P_2^H(r_1, r_2)}{P_2^H(r_1, r_2)} \right)_{r=0} \]
(20)
and
\[ G(\beta, Z) = \{0.121 - 0.016\beta^{-2} Z + 0.0458\beta^{-1} - 0.005\beta^{-3} Z\} \]
\[ \times \{1 + 1.1284\beta^{-1} + 0.3183\beta^{-2}\}^{-1} \]
(21)

If one now rewrites the above result in a different form, namely by approximating [21] the \( G \) functional with new parameters, then one finally obtains
\[ G = a \{1 + b \beta^{-1} Ze^{-c/\beta}\} \cdot \{1 + d \beta^{-1}\}^{-1} \]
(22)
with \( a, \ b, \ c \) and \( d \) determined from the previous general expression. After a few further manipulations one arrives at the final formula for the approximate CS correlation energy

\[
E_{\text{corr}}^\text{CS} = -a \int \rho(R)((1 + b\rho(R))^{-2/3}Z_{e}^{-\omega(R)^{-1/3}} \cdot (1 + d\rho(R))^{-1/3})^{-1} dR
\]  

(23)

where \( a = 0.04981, \ b = 0.066, \ c = 0.253 \) and \( d = 0.349 \). The above model has successfully predicted correlation energies for several atoms and molecules [22] (for a comparative study see ref. 26). In the case of continuum electrons being scattered by the bound electrons of an atom or a molecule, one can employ this result to describe the short-range polarization of the target electrons as given by the local functional derivative of the corresponding correlation energy obtained from eqn. (23). One can then use second-order perturbation expansions to describe its long-range behaviour. The final total correlation–polarization potential \( V_{\text{CP}}(r_{N+1}) \) then depends on the coordinate of the scattered electron \( r_{N+1} \) corresponding to the chosen spatial value of the total electron density

\[
V_{\text{CP}}^\text{CS}(r_{N+1}) \approx \frac{\partial}{\partial \rho(r)} E_{\text{corr}}^\text{CS}[\rho(r)] \bigg|_{r=r_{N+1}} \quad r_{N+1} < r_c
\]

(24a)

\[
\approx V_{\text{Pol}}^d(r_{N+1}) \quad r_{N+1} > r_c
\]

(24b)

where the dipole contribution to the asymptotic polarization term is given by eqn. (3). Equation (24a) is used in the inner region \( (r_{N+1} \leq r_c) \), whereas eqn. (24b) is employed in the outer asymptotic region \( r_{N+1} > r_c \). The value of \( r_c \) is chosen as the crossing distance between the value of the functional derivative of \( E_{\text{corr}}^\text{CS} \) and the value of the dipole–polarization term. Thus, one implies the non-adiabatic corrections to the asymptotic expansion begin to act within the spatial volume for which the short-range correlation correction to the HF energy of the \((N+1)\)-electron system can be used.

The success of eqn. (23) for bound electrons could be justified in more detail by examining how the electron–electron scattering within the bound electron density affects the different terms which contribute to the electronic energy.

The modified correlation formula

The factor \( q(R) \) in eqn. (8) is supposed to give a measure of the local accuracy of the zeroth order wavefunction being chosen in eqn. (4) with respect to the HF approximation for it [23]

\[
q(R) = 2.29 
\times \left( 1 + 7 \left\{ \frac{[-h(r_1) - h(r_1)]p_2^s(r_1, r_2, r_1', r_2')}{p_2^s(r_1, r_2)} - \frac{[-h(r_1) - h(r_2)]p_2^\text{HF}(r_1, r_2, r_1', r_2')}{p_2^\text{HF}(r_1, r_2)} \right\} \right)^2
\]

(25)
The factor 2.29 has been obtained by reproducing the $E_{\text{corr}}$ value of the He atom [21]. Thus, the above equation shows that the multiplicative term within the brackets is zero if $\psi^0 \equiv \psi^{\text{HF}}$.

In a further study on the various contributions to the total exact energy of the He atoms [27], it was pointed out, however, that the contribution from the electron–electron interaction term is almost twice the value of the $E_{\text{corr}}$ for that system. It therefore follows that if one requires eqn. (23) to reproduce the full correlation in the case of He, one might thus underestimate the corresponding contribution of the Coulomb hole. The latter quantity is defined as the difference between normalized distribution functions for the interelectronic distance as given by the correlated and by the HF wavefunctions of He [27].

The subsequent modification of the parametrization of $q$ in eqn. (8) in order to also provide the correct description of the Coulomb hole brings its new value to 1.76 instead of 2.29. Correspondingly, the other four parameters of eqn. (23) all become slightly modified as follows: $a = -0.0578; b = 0.062; c = 0.253; d = 0.543$. This physical correction, however, does not appreciably change the $E_{\text{corr}}$ values given by eqn. (23) for several systems and therefore does not alter the overall efficacy of the CS functional form. In what follows we use the latter modification because of its more realistic selection of the $q$ factor in eqn. (8). The basic ingredient of the present treatment of short-range correlation potential is the selection of the total electronic density for the system at hand from which to start the evaluation of electron–electron effects. However, one could continue the above analysis even further and obtain a more complete functional dependence of the sought CE on the initial electronic densities. An example of this procedure is discussed next.

The Lee–Young–Parr (LYP) correlation as a local density functional

The formula of eqn. (23) for the short-range correlation energy is not a pure density functional because of the direct dependence of the gradient operator results on the individual orbitals from HF wavefunctions.

One could, however, go further in that direction by employing local kinetic-energy densities and therefore obtain correlation energy functionals in a more transparent formulation [28]. This was done by Lee, Young and Parr (LYP) [28] using an exponential approximation for the density matrix that had been shown earlier to be equivalent to Wigner's distribution [29,30]. LYP therefore produced density functional for the correlation energy of eqn. (23) by using first a local formulation for the kinetic energy part of the density and then by expanding further the Hartree–Fock local kinetic density. In the following we call their formulation the LYP functional for the short range correlation energy. The first step is to rewrite
the gradient operator of eqn. (20) as
\[ \nabla_R \rho_*^{\text{HF}}(R, r)|_{r=0} = \rho(R) \{ t_{\text{HF}}(R) - 2t_w(R) \} \] (26)
where \( t_{\text{HF}} \) and \( t_w \) are now local kinetic-energy densities, for HF systems and Weitaker systems respectively [31].

\[
t_{\text{HF}}(R) = \frac{1}{8} \sum_{T} \frac{|
abla \rho_1(R)|^2}{\rho_1(r)} - \frac{1}{8} \nabla^2 \rho(R) \] (27a)
\[
t_w(R) = \frac{1}{8} \frac{|
abla \rho(R)|^2}{\rho(R)} - \frac{1}{8} \nabla^2 \rho(R) \] (27b)

where the summation of eqn. (27a) extends over the occupied HF orbitals of the target. The insertion of such local expressions in eqn. (23) provides therefore a different formula, easier to evaluate, and also allows its simpler extension to open-shell systems [28].

\[
E_{\text{CS-LYP}}^{\text{corr}} = -a \left( \rho(R) + b \rho(R)^{-2/3} [t_{\text{HF}}(R) - 2t_w(R)] \right) \frac{e^{-\rho(R)^{-1/3}}}{1 + d \rho(R)^{-1/3}} \text{d}R \] (28a)

\[
E_{\text{CS-LYP}}^{\text{corr}} = -a \left\{ \rho(R) + 2b \rho(R)^{-5/3} [\rho_\alpha(R) t_{\text{HF}}^\alpha(R) + \rho_\beta(R) t_{\text{HF}}^\beta(R)] \right. \\
- \left. \rho(R) t_w(R) \right\} \frac{e^{-\rho(R)^{-1/3}}}{1 + d \rho(R)^{-1/3}} \right\}^{-1} \gamma(R) \text{d}R \] (28b)

where
\[
\gamma(R) = 2 \left\{ 1 - \frac{\rho_\alpha^2(R) + \rho_\beta^2(R)}{\rho^2(R)} \right\} \] (29)

Here the indexes \( \alpha \) and \( \beta \) refer to densities for electrons with spins \( \alpha \) and \( \beta \) respectively. The four parameters \( a-d \) are the same as in eqn. (23) and the two different functional forms of the above now refer to closed-shell systems (eqn. (28a)) and open-shell systems (eqn. (28b)). The main modification comes from having rewritten the kinetic energy operators, so one expects eqns. (28) and (29) to give the same results as \( E_{\text{CS}}^{\text{corr}} \) of eqn. (23); this was indeed the result when actual comparisons were made [28].

If one adopts the simpler view that the orbitals employed in eqn. (27a) are the Kohn–Sham orbitals of the system [32], the eqns. (28) and (29) can be regarded as LDF formulae. We return to this point in more detail, but for now suffice it to say that it is more rigorous to recognize instead the above orbitals as being given by HF densities and to perform an explicit gradient expansion about the TF kinetic energy expressions [28]. Thus, because the TF kinetic-energy density is given by the familiar formulae [16,17]
\[
t_{\text{TF}}(R) = C_F \rho(R)^{5/3} \] (30a)
\[
C_F = \frac{3}{10} (3\pi^2)^{2/3} \] (30b)

the conventional closed-shell gradient expansion of \( t_{\text{HF}} \) gives, to zeroth
order \([33,34]\)

\[
t_{HF}(R) = t_{TF}(R) = C_F \rho(R)^{6/3}
\]

and to second order

\[
t_{HF}(R) = t_{TF}(R) + \left\{ \frac{1}{6} t_w(R) + \frac{1}{18} \nabla^2 \rho(R) \right\}
\]

The corresponding open-shell formulae can also be readily obtained by using the expressions \([35]\)

\[
t^a_{HF}(R) = \frac{1}{2} t_{HF} [R, 2 \rho_a(R)]
\]

\[
t^b_{HF}(R) = \frac{1}{2} t_{HF} [R, 2 \rho_b(R)]
\]

The correlation energy can now be explicitly obtained as a local density functional by modifying the original \(E_{\text{corr}}^{\text{CS}}\) of eqn. (23). The new functional expressions are called hereafter the \(E_{\text{corr}}^{\text{LYP}}\) correlation energies

\[
E_{\text{corr}}^{\text{LYP}} = -a \left[ 1 + d \rho^{-1/3} \right]^{-1} \cdot \left\{ \rho + \frac{b \rho^{-2/3}}{C_F \rho^{6/3}} - 2 t_w + \left( \frac{1}{6} t_w + \frac{1}{18} \nabla^2 \rho \right) e^{-c \rho^{-1/3}} \right\} dR
\]

\[
E_{\text{corr}}^{\text{LYP}} = -a \left[ \gamma(R) \left[ 1 + d \rho^{-1/3} \right]^{-1} \cdot \left\{ \rho + 2 b \rho^{-5/3} \cdot \left[ 2^{2/3} C_F \rho^{6/3} \right. \right. \\
+ 2^{2/3} C_F \rho^6_b \right. - \rho t_w + \left. \frac{1}{6} (\rho_x t^x_w + \rho_y t^y_w) + \frac{1}{18} (\rho^2_x + \rho^2_y) \right\] e^{-c \rho^{-1/3}} \right\} dR
\]

The zeroth-order formulae are obtained by cancelling in each equation the terms within the parentheses. Equation (34a) applies to closed-shell targets, whereas eqn. (34b) refers to open-shell targets. It is interesting to note that the above functional expressions provide excellent representations of actual correlation energies, in some cases showing even better agreement with exact values than the \(E_{\text{corr}}^{\text{CS}}\) formula of eqn. (23) \([28]\). The advantage of this functional alternative is that everything is now given as a functional of the electron density and therefore it provides an even more transparent way of evaluating the \(V_{CP}\) potential required in the scattering studies. Thus, one can write, as in eqn. (24), that \([28]\)

\[
V_{\text{CP}}^{\text{LYP}} (r_{N+1}) = \frac{\partial}{\partial \rho} E_{\text{corr}}^{\text{LYP}} = -a (F'_1 \rho + F_1) - ab C_F \rho^{5/3} (G'_1 \rho + \frac{8}{3} G_1) - \frac{ab}{4} [G'_1 \rho |\nabla \rho|^2 \\
+ G'_1 (3 |\nabla \rho|^2 + 2 \rho \nabla^2 \rho) + 4 G_1 \nabla^2 \rho] - \frac{ab}{72} [3 G'_1 \rho |\nabla \rho|^2 \\
+ G'_1 (5 |\nabla \rho|^2 + 6 \rho \nabla^2 \rho) + 4 G_1 \nabla^2 \rho] \quad \text{for } r_{N+1} < r_c
\]

where

\[
F'_1 [\rho(R)] = [1 + d \rho^{-1/3}]^{-1}
\]

\[
G'_1 [\rho(R)] = F_1 (\rho)^{-5/3} e^{c \rho^{-1/3}}
\]
and the symbols with the upper primes and double primes correspond to their first and second derivatives with respect to $\rho(R)$ respectively. A similar expression can also be obtained for the open-shell targets, from the corresponding open-shell equations given previously. The functional form, after the $r_c$ crossing, is taken to be once again the asymptotic second-order perturbation expression of eqn. (24b).

**Correlation forces from electron gas models**

The previous derivatives of correlation forces were based either on a specific type of correlated wavefunction ($E_{\text{corr}}^{\text{CS}}$) or on the use of LDF forms that began with HF densities to obtain the required functional expressions (e.g. $E_{\text{corr}}^{\text{LYP}}$). The more commonly used LDF expressions, however, start by using the electron gas as a reference system and later modifying the actual functional form [36,37].

One of the most recent proposals, for instance, is due to Becke [38] and suggests a functional form of the correlation energy that considers the short-range effects explicitly in the two-particle density matrix. This model treats opposite-spin and same-spin pairs of electrons separately and also tries to properly include correlation contributions to the kinetic energy. It starts from an approximate expression for the exchange-correlation hole and provides a non-local expression for a non-uniform electron gas. The required parameters in the model expansion were obtained by fitting the HF energies of the rare gas atoms and by adjustment to the "experimental" correlation energies of He and Ne.

In a rather extensive comparison of the relative performances of $E_{\text{corr}}^{\text{LYP}}$ and the above (called $E_{\text{corr}}^{\text{CM}}$), the ionization energies, electron affinities and dissociation energies for several atomic systems were calculated [39]. It was indeed found that the two functional expressions provided very similar results across the whole series of compounds examined. Our present interest is in the analysis of LDF approaches in evaluating short-range correlation potentials, so we discuss later only those calculations using local-density-functional forms of such potentials.

The simplest way of obtaining short-range correlation forces is possibly by using the uniform electron gas approximation. Thus, one may begin by using the expression of Hohenberg and Kohn [14] and Kohn and Sham [32] for the total energy of a many-electron system (eqn. (37))

$$E_{\text{TOT}} = T_0 + \int \rho(r) V_{\text{ext}} \, dr + \frac{1}{2} \int \int \frac{\rho(1) \rho(2)}{r_{12}} \, d1 \, d2 + E_{\text{xc}}$$

In this expression, $T_0$ is the kinetic energy of a system of non-interacting particles, $V_{\text{ext}}$ is the applied external potential and $E_{\text{xc}}$ is the exchange-correlation energy that can be written as a unique functional of the spin
densities $\rho_\alpha$ and $\rho_\beta$. The corresponding Kohn and Sham orbitals are determined, as non-interacting particles, by a self-consistent one-body potential

$$V_0^{\alpha,\beta} = -\frac{1}{2} \nabla \psi_i^{\alpha,\beta} + V_0^{\alpha,\beta} \psi_i^{\alpha,\beta} = \epsilon_i^{\alpha,\beta} \psi_i^{\alpha,\beta} \quad (38)$$

where

$$V_0^\beta = V_{\text{ext}} + V_{\text{el}} + V_{\text{xc}} \quad (39)$$

and

$$V_{\text{el}}(1) = \int \frac{\rho(2)}{r_{12}} \, d2$$

$$V_{\text{xc}}^{\alpha} = \frac{\partial}{\partial \rho_\alpha} E_{\text{xc}} \quad (40b)$$

It is often convenient to separate exchange and correlations components in eqn. (37) and, consequently, obtain two separate functional derivatives for eqn. (40b). Moreover, each of the one-body potentials of eqn. (39) can be written as a sum of contributions which are also unique functionals of the electron density [12]. Thus, one can write for the $E_{\text{xc}}$ of eqn. (37)

$$E_{\text{xc}} = E_x + E_c = \int \rho(r) \epsilon_x \, dr + \int \rho(r) \epsilon_c \, dr \quad (41)$$

where $\epsilon_x$ and $\epsilon_c$ provide the independent single-particle contributions to exchange and correlation energies. Hence, the corresponding effective potential of eqn. (39) can be obtained as

$$V_{\text{xc}}^{\alpha} = \frac{\partial}{\partial \rho_\alpha} \left[ \rho_\alpha(r) \epsilon_x \right] + \frac{\partial}{\partial \rho_\alpha} \left[ \rho_\alpha(r) \epsilon_c \right] \quad (42)$$

When one uses a homogeneous electron gas, the above functional derivatives can be performed very easily [32] and therefore one obtains an interpolation formula for the free electron gas (FEG) model for the correlation potential

$$V_{\text{corr}}^{\text{FEG}} = \begin{cases} 0.0311 \ln r_s - 0.0584 + 0.006 r_s \ln r_s + 7.015 r_s & (r_s \leq 0.7) \\ -0.07356 + 0.02224 \ln r_s & (0.7 \leq r_s \leq 10.0) \\ -0.584 r_s^{-1} + 1.988 r_s^{-3/2} - 2.450 r_s^{-2} - 0.733 r_s^{-5/2} & (r_s > 10) \end{cases} \quad (43)$$

where

$$r_s = [3/4 \pi \rho(r)]^{1/3}$$

Thus, the short-range correlation potential is obtained here directly as a functional derivative at low electron densities (large $r_s$), large electron densities (small $r_s$) and interpolated linearly between the two regions [40,41]. Such an approximation, however, clearly fails when the impinging
electron is beyond the outer edge of the atom or molecule because the FEG approximation makes no allowance for polarization of the bound electrons caused by the presence of an external particle. Thus, at the outer crossing \( r_c \) introduced in eqn. (24), one replaces the short-range expression of eqn. (43) by the standard perturbative expansion form discussed previously. This is the simplest prescription for joining the FEG potential with the long-range polarization potential and (though to be thought of as an ad hoc procedure) it is clearly defined and free of adjustable parameters. The main drawback, as we will discuss below, is the rather approximate nature of the FEG model and therefore its well-known inaccuracy when describing molecular properties.

A more efficient fit for the correlation energy, still using the FEG reference density, was produced a few years back [37] and yielded a different functional form

\[
V_{\text{FEG-PZ}}(r_{NH}) = \begin{cases} 
0.0311 \ln r_s - 0.0584 + 0.00133 r_s \ln r_s - 0.0084 r_s & (r_s < 1.0) \\
\gamma (1 + \frac{7}{6} \beta_1 r_s^{1/2} + \frac{4}{3} \beta_2 r_s) & (r_s \geq 1.0)
\end{cases}
\]

where \( \gamma = 0.1423 \), \( \beta_1 = 1.0529 \) and \( \beta_2 = 0.3334 \).

The new interpolation, as we discuss below, generally results in a weaker short-range correlation potential, thus correcting the results of eqn. (43) in the right direction.

**RESULTS AND DISCUSSION**

In the previous section we have shown how one could take advantage of currently developed DFT methods for calculating ground electronic states of atoms, molecules and solids, and use them to deal with the essentially inhomogeneous behaviour of an electron scattered by atoms and molecules in the short-range region of configuration space, where strongly non-adiabatic dynamical effects prevent the use of the more convenient asymptotic perturbation theories.

We have focussed our attention on ways of dealing with electron–electron scattering effects during elastic collisions and on the possible forms that a LDF approximation can take when describing such effects. The situation is not exactly the same as in a conventional chemical bond (where all particles are bound within the fixed-nuclei B–O configuration representing that particular molecule) but most of the terminology and effects used for chemical forces is currently employed in describing the (mostly chemical) consequences of the scattering of low-energy electrons by molecular (and atomic) targets. In what follows we report some preliminary application of the previous study on the calculation of correlation potentials for electron scattering from rare gases.
The wavefunctions employed were given as a single determinant (SD) representation, where each orbital was obtained by an expansion over STO functions, with the usual SCF procedure for the coefficients [42]. Only closed-shell electronic ground states are considered in the examples below.

In order to make the discussion meaningful, we have carried out calculations with:

(i) the correlation potentials employed earlier for the rare gas systems, using the FEG approximation [40];
(ii) the correlation potentials obtained from a specific “ansatz” for the initial wavefunction and using HF density matrices, i.e. the $V_{cs}^{corr}$ of eqn. (24);
(iii) the correlation potentials obtained from a full DFT description of the previous derivation, i.e. the $V_{LYP}^{corr}$ of eqn. (35a).

All the above calculations are then compared with the long-range perturbation expansion which is here given by its leading term only, i.e. the dipole polarizability term of eqn. (3). The latter comparison, in fact, allows one to see fairly directly the effects of non-adiabatic corrections in the short-range region.

Figure 1 reports the correlation potentials computed for the He target over the whole region of interaction: $V_{cor}^{FEG}$ is clearly seen to be the strongest of them all in the inner region and crosses the asymptotic potential at the
smallest $r_c$ value ($\approx 1.7a_0$). In contrast, the LDF formulation of the LYP potential (---) is evidently providing here a non-adiabatic correction which is somewhat less than that given by the $V_{\text{corr}}^{\text{FEG}}$ potential (-----), because the latter shows the weakest form of correlation potential at very short distances. In other words, the damping of the adiabatic, long-range polarization by short-range electron-electron correlation effects is handled here very differently by the three chosen functionals. The simplest FEG model is obviously correcting the $V_{\text{pol}}$ divergence rather weakly, thus producing an interaction that is still too strong as the electron-target distance goes to zero. This feature has also been found in previous studies with this correlation potential [40,41]. The correlated function which provides the "ansatz" for the $V_{\text{corr}}^{\text{LDF}}$ interaction, however, appears to introduce cusp effects which are too strong at very short distances and dampens there too rapidly the asymptotic polarization term. It is interesting to note at this point that the relatively small errors in correlation energy given by this model potential [28] appears to have been nearly always negative, i.e. slightly too large values of correlation energies were produced by the $E_{\text{corr}}^{\text{CS}}$ in nearly all cases examined. Hence, one can thus explain the excessive damping shown by our correlation potential in Fig. 1, as $r$ goes to zero.

It is, however, very comforting to see that both correlation potentials which go beyond the FEG model behave very similarly up to the inner crossing ($r_c$) with the polarization potential; and both show a marked reduction of strength with respect to the FEG correlation. In the outer region of the interaction (as shown in Fig. 2) one sees that the $V_{\text{corr}}^{\text{LYP}}$ potential (-----) now follows the polarization potential very closely and does so from $r \approx 4a_0$, while the correlation from the FEG model and the correlation based on the CS functional formula (with the CC modification, ····) are both too strong in the outer region and therefore need to be replaced earlier on by the more realistic $V_{\text{pol}}$ (-----).

The corresponding comparison for the Ne target is shown in detail in Fig. 3, where the same three correlation potentials discussed here are reported. In the very short-range region of interaction (Fig. 3(a)) the results from $V_{\text{corr}}^{\text{FEG}}$ once again dampen too quickly the asymptotic behaviour of polarization, whereas the FEG modelling of short-range correlation (-----) produces an overall interaction which is excessively strong. The interaction region just outside the values of $r_c$ for all potentials is shown in Fig. 3(b), to emphasize the relative strength of the three models in describing the outer edge of the interaction. The LDF model of LYP appears to be the only one that carries the short-range effects correctly out to the region of asymptotic polarization. Its different handling of kinetic energy correlation effects via the local density functional approach is obviously effective, the CS treatment still omits (as pointed out previously [38]) kinetic energy corrections. Such differences of behaviour are even more intriguing
Fig. 2. As for Fig. 1, showing the radial region outside the crossing values of Table 1 (for He targets). For an explanation of the symbols see Fig. 1.

when one moves out to the long-range values of relative distances (Fig. 3(c)). One sees in Fig. 3(c) how $V_{\text{corr}}^\text{LYP}$ follows the behaviour of $V_{\text{Pol}}$ very closely out to about 10–11$a_0$, as shown by (—) and (——). Thus, one may surmise that the LDF treatment of the short-range correlation (with local kinetic energy densities) goes very smoothly out to the adiabatic asymptotic region and therefore is likely to treat the $V_{cp}$ interaction realistically even in the intermediate region outside the first crossing with $V_{\text{Pol}}$.

The difference in behaviour of the CS formula and the LYP functional in describing short-range correlation forces becomes less in the region $r < r_c$, as one is moving to the heavier atoms with larger number of electrons. The results for Ar, Kr and Xe are shown in Figs. 4, 5 and 6 for all three correlation potentials. They are again compared with the behaviour of their respective asymptotic polarization terms (——).

As for Ar targets, for instance, the results shown in Fig. 4 demonstrate that for distances up to about 2.5$a_0$ the two potential functions are indeed very similar, whereas at very short radial values, $V_{\text{corr}}^\text{CS}$ becomes repulsive and $V_{\text{corr}}^\text{LYP}$ goes to zero: it is in the region closest to the nuclei that the different treatment of kinetic energy is expected to mostly affect the two functional models. In contrast, one also sees that $V_{\text{corr}}^\text{CS}$ connects nicely with $V_{\text{Pol}}$ at its inner crossing ($r_c \approx 3.8a_0$), whereas $V_{\text{corr}}^\text{LYP}$ does so at its outer crossing with $V_{\text{Pol}}$ ($r_c \approx 5.3a_0$). Both potentials indeed contain distortion effects on the initial HF wavefunction caused by correlation forces and,
Fig. 3. Computed correlation potentials for electron scattering from Ne targets: (a) general view of the whole radial range of the interaction; (b) radial region just outside the crossings of the short-range potentials; (c) asymptotic region of all the computed potentials. For an explanation of the symbols see Fig. 1.
Fig. 4. Computed correlation potentials for electron collisions with Ar atoms. For an explanation of the symbols see Fig. 1.

Fig. 5. Correlation potentials computed for the scattering of electrons from Kr atoms. For an explanation of the symbols see Fig. 1.
therefore, it is reassuring to see that they both smoothly connect with the asymptotic polarization term as the relative distance increases.

For the two heaviest rare gases (Kr and Xe) the calculations reported in Figs. 5 and 6 confirm the differences in behaviour already found, for the three correlation potentials. The FEG model consistently produces an interaction which is too strong at short distances, whereas $V_{CS}^{\text{corr}}$ possibly dampens the asymptotic polarization too much; both $V_{CS}^{\text{corr}}$ and $V_{LYP}^{\text{corr}}$ show oscillations in the short-range regions, showing the effects of the various inner shells on the total-density behaviour. This is what one expects for a non-homogeneous electron density; no oscillations are given by the simpler FEG modelling of the target densities.

In conclusion, the present study has shown the feasibility of using DFTs for the treatment of non-adiabatic effects in electron-molecule collisions. When exchange effects and Coulomb interactions are treated exactly (as in the so-called exact-static-exchange (ESE) scattering equations [3]), the present approach provides a very effective method for correcting (in the overlap region) the false behaviour of the induction series of eqn. (1). Moreover, by comparing different ways of producing such a functional dependence, we have also demonstrated the following.
TABLE 1

Radial values of the correlation potential crossings with the asymptotic dipole polarization potentials of the rare gas targets (a.u.)

<table>
<thead>
<tr>
<th>Rare gas</th>
<th>$V_{\text{corr}}^{\text{a}}$</th>
<th>$V_{\text{corr}}^{\text{b}}$</th>
<th>$V_{\text{corr}}^{\text{c}}$</th>
<th>$V_{\text{corr}}^{\text{d}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.11</td>
<td>1.85</td>
<td>1.67</td>
<td>6.75</td>
</tr>
<tr>
<td>Ne</td>
<td>2.86</td>
<td>2.15</td>
<td>1.95</td>
<td>6.25</td>
</tr>
<tr>
<td>Ar</td>
<td>3.86</td>
<td>3.15</td>
<td>2.87</td>
<td>5.32</td>
</tr>
<tr>
<td>Kr</td>
<td>4.33</td>
<td>3.20</td>
<td>3.23</td>
<td></td>
</tr>
<tr>
<td>Xe</td>
<td>4.95</td>
<td>3.65</td>
<td>3.67</td>
<td></td>
</tr>
</tbody>
</table>

*From eqn. (24) of the text; CC modification factors.

bFrom eqn. (35) of the text.

cFrom eqn. (43) of the text.

dOuter second crossing from eqn. (35) of the text.

(i) The use of a simple electron gas model for the density produces damping behaviour which is not effective enough, generating a correlation potential which is too strong in the short-range region.

(ii) The use of a specific correlated wavefunction to construct the short-range functional (as in $V_{\text{corr}}^{\text{b}}$) seems to show more realistic behaviour in the inner region but reduces polarization in the intermediate region to very small values. For higher-Z nuclei, however, it connects very smoothly with the asymptotic coefficient of the induction series of eqn. (1).

(iii) The further introduction of local-density expressions for the kinetic energy terms, producing a correlation potential which has a genuine LDF form, is implemented in the $V_{\text{LYP}}^{\text{corr}}$ of eqn. (35) and the present results show it to be possibly the best description of both short- and intermediate-range regions of the correlation. Its inner crossings with $V_{\text{pol}}$ are always smaller than those from $V_{\text{CS}}^{\text{corr}}$ (shown in Table 1) indicating a larger overall correlation potential in the short- and intermediate-range distances.

All the above potential functions are quite easy to implement numerically can be straightforwardly extended to non-linear systems; they can be introduced in the quantum coupled equations of scattering without too much effort [5,43]. Specific results in that direction are currently in preparation by our group.

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