
Exchange-Correlation Energies and Correlation Holes for Some Two- and Four-Electron Atoms along a Nonlinear Adiabatic Connection in Density Functional Theory

R. POLLET,¹ F. COLONNA,¹ T. LEININGER,² H. STOLL,³
H.-J. WERNER,³ A. SAVIN¹

¹Laboratoire de Chimie Théorique (CNRS et Université Pierre et Marie Curie), Paris, France

²Laboratoire de Physique Quantique (CNRS et Université Paul Sabatier), Toulouse, France

³Institut für Theoretische Chemie (Universität Stuttgart), Stuttgart, Germany

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ABSTRACT: The adiabatic connection procedure of density functional theory has been applied to two- and four-electron atomic systems by following a nonlinear path that leads from the noninteracting Kohn–Sham reference system to the physical one. We have calculated the exchange and correlation energies as the interaction strength is increased, as well as the densities of the corresponding correlation holes. © 2002 Wiley Periodicals, Inc. *Int J Quantum Chem* 91: 84–93, 2003

Key words: correlation holes; density functional theory; exchange-correlation energies; nonlinear adiabatic connection

Introduction

The adiabatic connection [1–3] offers the opportunity to understand and design approximate functionals for the exchange–correlation energy of density functional theory (DFT) [4]. The technique

involves linking the Kohn–Sham [5] noninteracting reference system to the fully interacting physical system, by switching on the electron–electron interaction. The only necessary assumptions are the adiabatic connectivity [6] and the choice of the path to be followed at constant density. Among all the possible adiabatic paths [7], a nonlinear one has been tested in this article.

We briefly describe the underlying theory and survey technical details. Then, beside the “exact”

Correspondence to: A. Savin; e-mail: andreas.savin@lct.jussieu.fr

calculation of the exchange and correlation energies of a few systems, we focus on the correlation holes (see, e.g., Ref. [8]), because an understanding of these can be a starting point for the elaboration of new exchange-correlation functionals (see, e.g., the Taylor expansion of Becke [9] or the real-space cut-off procedure of Perdew [10]).

Theory

In the conventional application of the adiabatic connection procedure [11, 12], the electron–electron interaction is switched on by using a linear interpolation, but alternative paths exist. For example, we can make use of the error function and define

$$\hat{V}_{ee}^\lambda = \frac{1}{2} \sum_{i \neq j}^N \frac{\text{erf}(\lambda|r_i - r_j|)}{|r_i - r_j|} \quad (1)$$

where the interaction strength λ lies between 0 (Kohn–Sham system) and ∞ (physical system). Its attractive features have already been discussed by Yang [7]. Furthermore, it can give new insights into a recent method that combines short-range density functionals with long-range configuration interaction [13–17]. Adiabatic connection is indeed a rigorous formulation of such a coupling, and different paths will obviously produce different short-range exchange-correlation energies (at intermediate interaction strengths). One can then observe that approximations, for instance, LDA, can be more accurate for some paths [18].

We start by defining a λ -dependent Hamiltonian,

$$\hat{H}^\lambda = -\sum_i^N \frac{1}{2} \nabla_i^2 + \hat{V}_{ee}^\lambda + \sum_i^N v^\lambda(\mathbf{r}_i) \quad (2)$$

where the first term is the kinetic energy operator and the last term is the local potential associated with the system with partial electron–electron interaction. When $\lambda \rightarrow \infty$, $v^{\lambda \rightarrow \infty}$ will be the real external potential of the interacting system, whereas when $\lambda = 0$, $v^{\lambda=0}$ is identical to the Kohn–Sham potential. The potential v^λ has to be constructed so that it maintains the density equal to the physical one for all λ 's. This can be achieved by searching for the universal Legendre transform functional [19] (see also [20]),

$$F^\lambda[\rho] = \max_{v^\lambda} \left\{ E^\lambda[v^\lambda] - \int \rho(\mathbf{r})v^\lambda(\mathbf{r}) \, d\mathbf{r} \right\} \quad (3)$$

where

$$E^\lambda[v^\lambda] = \langle \Phi_{v^\lambda}^\lambda | \hat{H}^\lambda | \Phi_{v^\lambda}^\lambda \rangle \quad (4)$$

If the arbitrary density ρ is the physical one, we get at the end of the maximization process the potential v_{max}^λ and thus the ground-state wavefunction $\Phi_{v_{max}^\lambda}^\lambda$ of the system in partial interaction, which yields the density ρ .

As we know $\Phi_{v_{max}^\lambda}^\lambda$, we can now calculate the corresponding exchange and correlation energies. Because the density is constant, the λ -dependent correlation energy

$$E_c^\lambda = \langle \Phi_{v_{max}^\lambda}^\lambda | \hat{H}^\lambda | \Phi_{v_{max}^\lambda}^\lambda \rangle - \langle \Phi_{v_{max}^{\lambda=0}}^{\lambda=0} | \hat{H}^\lambda | \Phi_{v_{max}^{\lambda=0}}^{\lambda=0} \rangle \quad (5)$$

becomes

$$E_c^\lambda = \langle \Phi_{v_{max}^\lambda}^\lambda | \hat{T} + \hat{V}_{ee}^\lambda | \Phi_{v_{max}^\lambda}^\lambda \rangle - \langle \Phi_{v_{max}^{\lambda=0}}^{\lambda=0} | \hat{T} + \hat{V}_{ee}^\lambda | \Phi_{v_{max}^{\lambda=0}}^{\lambda=0} \rangle \quad (6)$$

$$= F^\lambda[\rho] - F^{\lambda=0}[\rho] - \langle \Phi_{v_{max}^{\lambda=0}}^{\lambda=0} | \hat{V}_{ee}^\lambda | \Phi_{v_{max}^{\lambda=0}}^{\lambda=0} \rangle \quad (7)$$

For the λ -dependent exchange energy, which depends only on the wavefunction of the noninteracting Kohn–Sham system, we get

$$E_x^\lambda = \langle \Phi_{v_{max}^{\lambda=0}}^{\lambda=0} | \hat{V}_{ee}(\lambda) | \Phi_{v_{max}^{\lambda=0}}^{\lambda=0} \rangle - U^\lambda \quad (8)$$

where $\Phi_{v_{max}^{\lambda=0}}^{\lambda=0}$ typically is a single Slater determinant of Kohn–Sham orbitals, and U^λ is the Hartree energy for the modified electron–electron interaction,

$$U^\lambda[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\text{erf}(\lambda r_{12})}{r_{12}} \, d\mathbf{r}_1 d\mathbf{r}_2 \quad (9)$$

From $\Phi_{v_{max}^\lambda}^\lambda$, we can also deduce the λ -dependent pair function [21],

$$P_2^\lambda(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int \dots \int |\Phi_{v_{max}^\lambda}^\lambda|^2 \, ds_1 \, ds_2 \, dx_3 \dots dx_N \quad (10)$$

where x represents both spatial and spin coordinates r and s . This pair function is the probability density to find simultaneously two electrons at points r_1 in the volume element dr_1 and r_2 in dr_2 , whatever their spin coordinates may be. The conditional probability is the density of the $N - 1$ remaining electrons at point r_2 when one reference electron is at point r_1 ,

$$P_{cond}^\lambda(2|1) = \frac{P_2^\lambda(r_1, r_2)}{\rho(r_1)} \quad (11)$$

The exchange-correlation density hole at point r_2 is then defined by

$$\rho_{xc}^\lambda(2|1) = P_{cond}^\lambda(2|1) - \rho(r_2) \quad (12)$$

This quantity is a measure of the influence of the reference electron on the density of the remaining electrons. With regard to these functions, we focus on the correlation part of Eq. (12),

$$\rho_c^\lambda(2|1) = \rho_{xc}^\lambda(2|1) - \rho_x(2|1) \quad (13)$$

where ρ_x is the density of the Fermi hole.

Technical Details

In practical applications, the method is composed of cycles in which a variation in the potential is immediately followed by a wavefunction calculation. Thus, the technique consists in allowing a “dialog” between a standard optimization program and an ab initio software.

To optimize the local potential, a convenient form was chosen, namely a spherical Gaussian basis,

$$v_{ps}(r) = \sum_i C_i r^{p_i} \exp(-\gamma_i r^2) + \frac{C}{r} \quad (14)$$

where r is the electron–nucleus distance, p_i are integers greater than or equal to -2 , γ_i are positive exponents and C may be deduced from asymptotical conditions. For example, the asymptotical behavior of the Kohn–Sham potential is given in Ref. [22]

$$\lim_{r \rightarrow \infty} v^{\lambda=0}(r) = \frac{-Z + N - 1}{r} \quad (15)$$

All these parameters are optimized by the simplex method with the help of the amoeba procedure [23]. A typical plot of the maximization of the functional (3) is represented in Figure 1 as an example.

A good criterion to judge the reliability of our optimized parameters is to evaluate the quantity used by Zhao and Parr [24],

$$\Delta = \frac{1}{2} \int \frac{[\tilde{\rho}^\lambda(r_1) - \rho(r_1)][\tilde{\rho}^\lambda(r_2) - \rho(r_2)]}{r_{12}} dr_1 dr_2 \quad (16)$$

where $\tilde{\rho}^\lambda$ denotes the output electron density produced at the end of the maximizing process. Even if accurate wavefunctions (hence, correlation energies) were obtained, the maximizing local potential v^λ cannot be unambiguously determined. For example, a shift by a constant over the physically relevant domain [25] or a rapidly oscillating perturbation [26] will not significantly affect the density.

As for the ab initio software, the Molpro [27] program was modified by adding the new bielectronic integrals [16]. All the studied systems belong to the isoelectronic series of helium and beryllium. For He, C^{4+} , and Ne^{8+} , the reference ground state density ρ and the ground-state energy E^λ were obtained by full configuration interaction, whereas a multireference configuration interaction [28, 29] was used for Be and Ne^{6+} . The basis functions are uncontracted even tempered gaussians, up to f functions (see Table I [11]).

Table II shows the accuracy of the maximizing potentials by listing the minimum, maximum and average values of the Parr criterion (16) for each system.

Results and Discussion

EXCHANGE AND CORRELATION ENERGIES

The λ -dependent exchange energies were calculated according to Eq. (8) for several interaction strengths. Figures 2 and 3 show these results for each series.

For the λ -dependent correlation energies, we performed nonlinear least-squares fitting of the curves with a fit limit set to $1e-08$, using Gnuplot [30], according to the three-parameter fit function

$$E_c^\lambda = \frac{\gamma x^2 + E_c x^4}{\alpha + \beta x^2 + x^4} \quad (17)$$

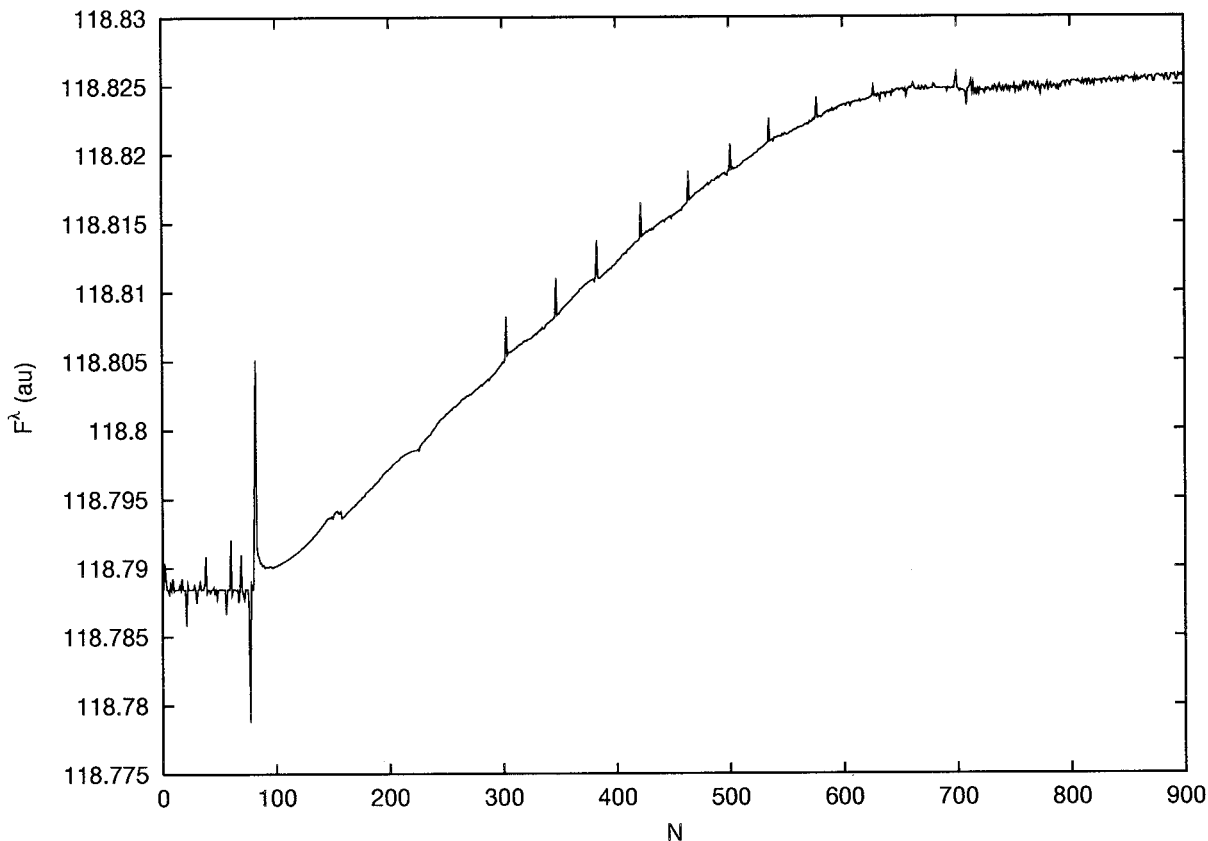


FIGURE 1. Maximization of the functional (3) by the simplex method for the Ne^{6+} system at $\lambda = 2$ over a number of iterations. When convergence is reached, $\Delta = 4.18 \cdot 10^{-9}$ [Eq. (16)].

where $x = \lambda/Z$. This function indeed satisfies known exact conditions. The first ones are obviously

$$E_c^\lambda = \begin{cases} 0 & \text{for } \lambda = 0 \text{ (Kohn-Sham system)} \\ E_c & \text{for } \lambda \rightarrow \infty \text{ (physical system)} \end{cases} \quad (18)$$

Moreover, applying the Hellmann-Feynman theorem to Eq. (6) leads to

$$\frac{dE_c^\lambda}{d\lambda} = \frac{1}{\sqrt{\pi}} \iint \rho(r_1) \rho_c^\lambda(2|1) \exp[-(\lambda r_{12})^2] dr_1 dr_2 \quad (19)$$

For $\lambda = 0$, the Gaussian function equals one and the correlation hole integrates to zero so that

$$\frac{dE_c^\lambda}{d\lambda} = 0 \quad \text{for } \lambda = 0 \text{ (Kohn-Sham system)} \quad (20)$$

TABLE I

Even-tempered Gaussian exponents obtained from rule $\alpha_n = \alpha_c \delta^{(2n-M-1)/2}$.

Functions Systems	<i>s</i>			<i>p</i>			<i>d</i>			<i>f</i>		
	<i>M</i>	δ	α_c	<i>M</i>	δ	α_c	<i>M</i>	δ	α_c	<i>M</i>	δ	α_c
He	21	2,1	40,0	7	2,1	3,0	5	2,1	3,0	3	2,1	3,0
C ⁴⁺	21	2,1	663,0	7	2,1	34,0	5	2,1	34,0	3	2,1	34,0
Ne ⁸⁺	21	2,1	2030,0	7	2,1	100,0	5	2,1	100,0	3	2,1	100,0
Be	21	2,1	4,0	9	2,1	1,0	5	2,1	1,0	3	2,1	1,0
Ne ⁶⁺	21	2,1	130,0	9	2,1	15,0	5	2,1	15,0	3	2,1	15,0

M is the number of Gaussians, α_c is the central exponent, and δ is the ratio between two consecutive exponents.

TABLE II
Minimum (Δ_{min}), maximum (Δ_{max}) and average (Δ_{avg}) Parr criteria (16) along the adiabatic connection.

Systems	Δ_{min}	Δ_{max}	Δ_{avg}^a
He	$2.15 \cdot 10^{-11}$	$8.74 \cdot 10^{-7}$	$1.07 \cdot 10^{-9}$
C ⁴⁺	$3.02 \cdot 10^{-13}$	$1.37 \cdot 10^{-10}$	$2.46 \cdot 10^{-12}$
Ne ⁸⁺	$1.72 \cdot 10^{-14}$	$6.36 \cdot 10^{-9}$	$3.40 \cdot 10^{-12}$
Be	$2.56 \cdot 10^{-9}$	$7.52 \cdot 10^{-8}$	$1.07 \cdot 10^{-8}$
Ne ⁶⁺	$1.47 \cdot 10^{-9}$	$6.83 \cdot 10^{-8}$	$8.48 \cdot 10^{-9}$

^a Equal to $10^{\sum \log(\Delta_i)/N}$, where N is the number of points along the adiabatic connection.

When $\lambda \rightarrow \infty$, we use the definition of the Dirac function,

$$\delta(r_{12}) = \lim_{\lambda \rightarrow \infty} \left\{ \frac{\lambda^3}{\pi^{3/2}} \exp[-(\lambda r_{12})^2] \right\} \quad (21)$$

so that

$$\frac{dE_c^\lambda}{d\lambda} \approx \frac{\pi}{\lambda^3} \int \rho(r_1) dr_1 \int \rho_c^\lambda(2|1) \delta(r_{12}) dr_2 \quad (22)$$

$$= \frac{\pi}{\lambda^3} \int \rho(r_1) \rho_c^\lambda(1|1) dr_1 \quad (23)$$

$$\approx \frac{\pi}{\lambda^3} \int \rho(r_1) \rho_c(1|1) dr_1 \quad (24)$$

where we use a Taylor expansion of the correlation hole near $\lambda \rightarrow \infty$ in Eq. (24). We thus obtain

$$\frac{dE_c^\lambda}{d\lambda} \propto \frac{\pi}{\lambda^3} \quad \text{for } \lambda \rightarrow \infty \text{ (physical system)} \quad (25)$$

In summary, the conditions (18), (20), and (25) are all satisfied by the fit function (17).

Figures 4 and 5 show these results for each series. The resulting fit errors and parameters are shown in Table III.

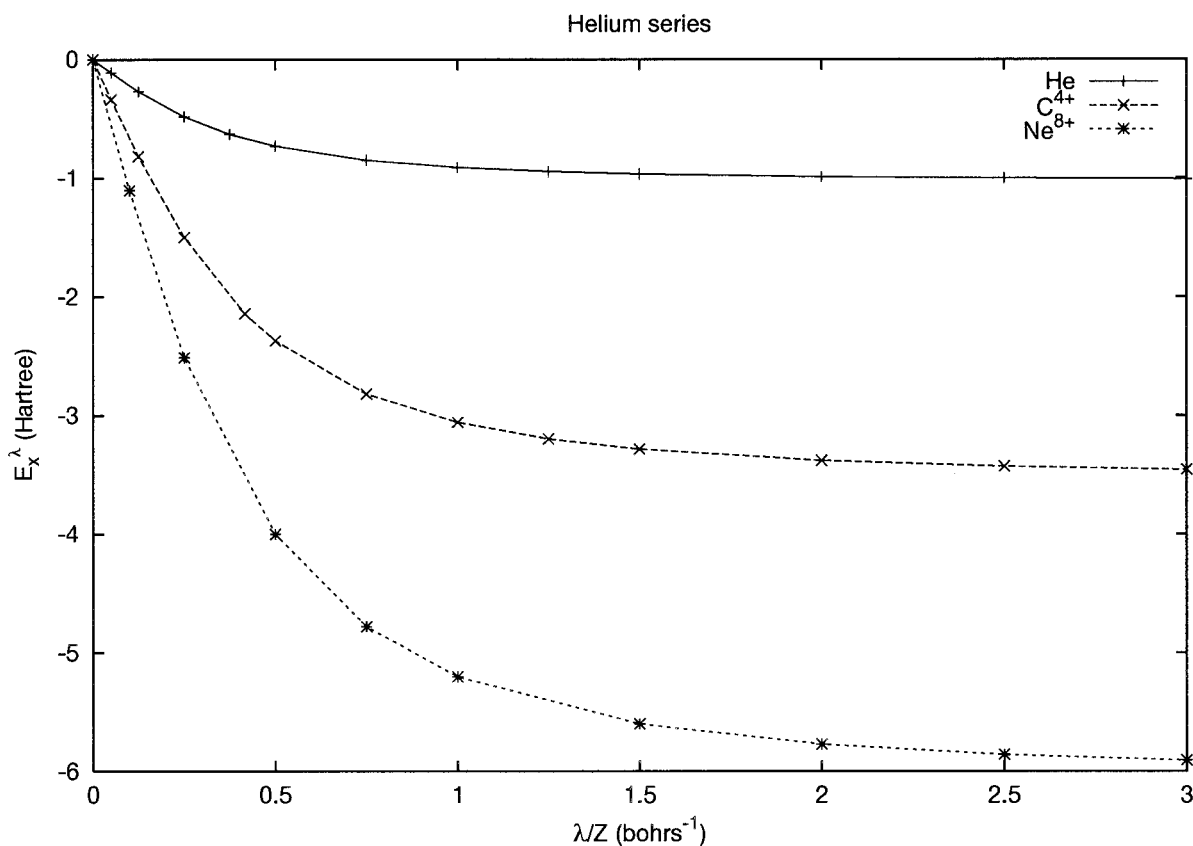


FIGURE 2. The λ -dependent exchange energies for systems belonging to the helium series (He, C⁴⁺, and Ne⁸⁺).

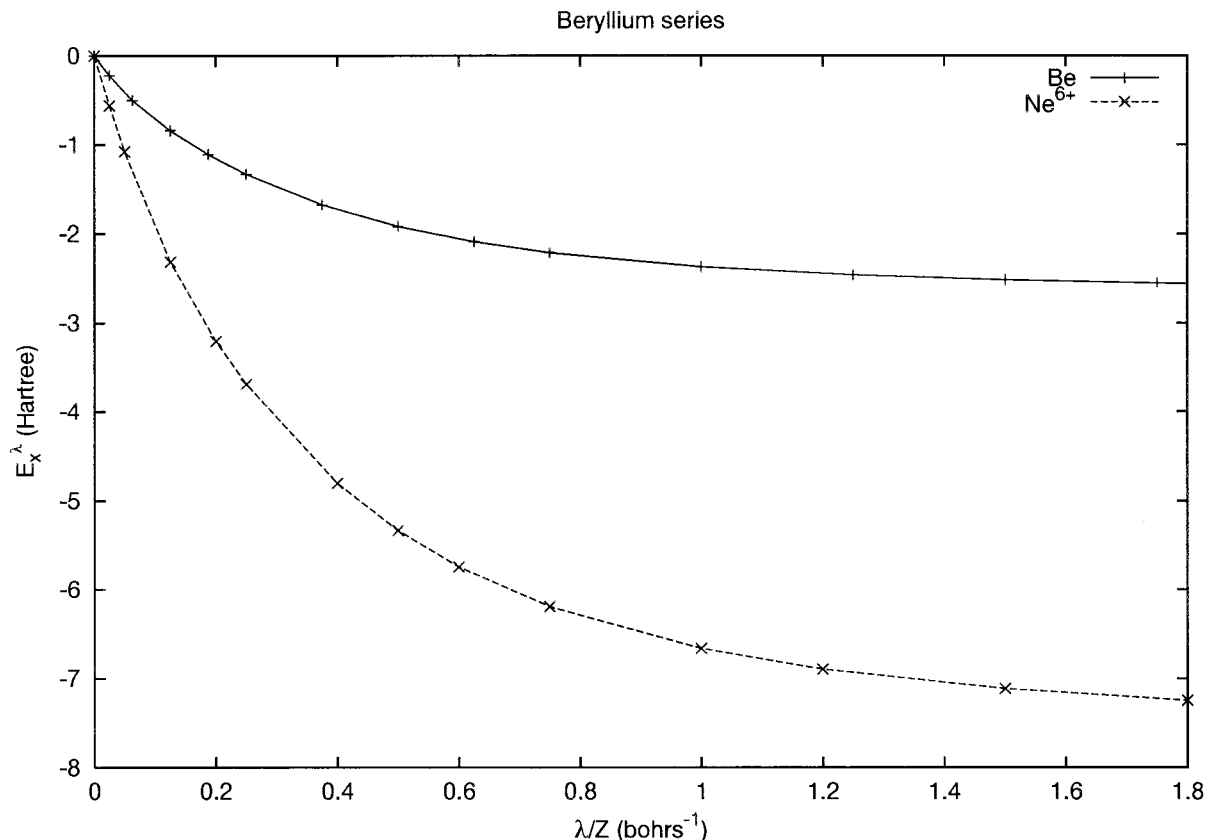


FIGURE 3. The λ -dependent exchange energies for systems belonging to the beryllium series (Be and Ne⁶⁺).

The asymptotical behavior (when $\lambda \rightarrow \infty$) of the λ -dependent correlation energies is different between the two series. In the case of the helium series, the three curves go to values that are close to each other, whereas for the beryllium series, the curves tend to values that are well separated. This feature can be explained by writing the electronic Hamiltonian in such a way that $1/r_{12}$ becomes a perturbation with factor $1/Z$ [31]. One can thus show that the second-order energetic correction is proportional to a constant in the case of the helium series, whereas the first-order energetic correction is linear with Z for the beryllium series.

CORRELATION HOLES

The Coulomb hole takes shape as the interaction strength λ is increased and recovers its final shape when $\lambda \rightarrow \infty$. This quantity is simple to obtain for two-electron systems such as the helium series. According to Eq. (13), the λ -dependent correlation hole is

$$\rho_c^\lambda(2|1) = \frac{P_2^\lambda(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} - \rho(\mathbf{r}_2) - \rho_x(2|1) \quad (26)$$

where the electron density equals

$$\rho(\mathbf{r}) = 2|\psi(\mathbf{r})|^2 \quad (27)$$

where ψ is the only occupied Kohn–Sham orbital,

$$P_2^\lambda(\mathbf{r}_1, \mathbf{r}_2) = 2|\Phi_{\sigma_{\max}}^\lambda(\mathbf{r}_1, \mathbf{r}_2)|^2 \quad (28)$$

and where

$$\rho_x(2|1) = -\frac{\rho(\mathbf{r}_2)}{2} \quad (29)$$

is the Fermi hole, which corresponds to $\lambda = 0$, as in a two-electron system exchange effects come only from the self-interaction correction. Moreover, the full CI wavefunction can be expanded in the natural orbital basis [32],

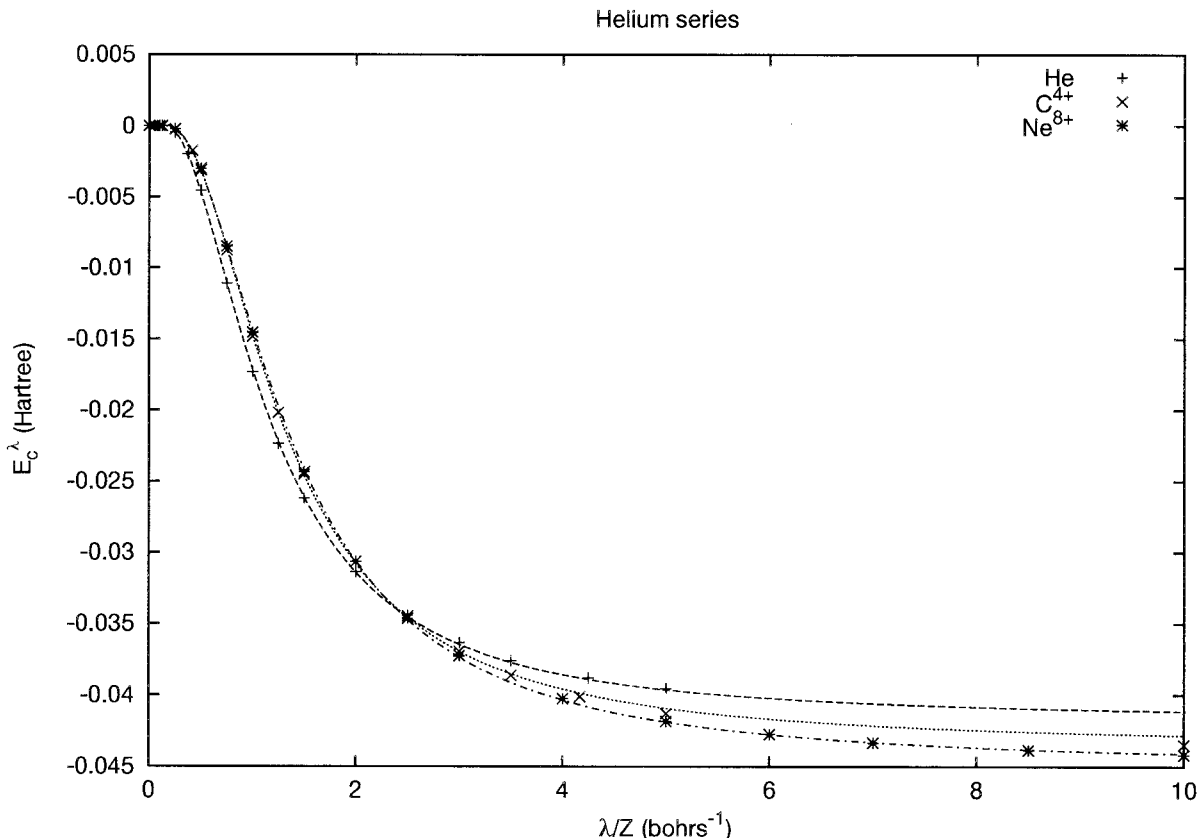


FIGURE 4. Fits of the λ -dependent correlation energies for systems belonging to the helium series (He, C $^{4+}$, and Ne $^{8+}$) according to the fit function (17).

$$\Phi_{v_{max}}^\lambda(\mathbf{r}_1, \mathbf{r}_2) = \sum_i d_i \zeta_i(\mathbf{r}_1) \zeta_i(\mathbf{r}_2) \quad (30)$$

where $d_1 = \sqrt{\lambda_1/2}$ and $d_i = -\sqrt{\lambda_i/2}$ for $i > 1$, λ_i being the occupation number of the orbital ζ_i .

Correlation holes for He have been studied for two positions of the reference electron. For the first series (when the reference electron is at 0.85 a.u. from the nucleus), we give Figure 6, corresponding to a weak interaction strength (for $\lambda = 0.1$, where the amplitude equals 10^{-4} a.u.), as the shape basically remains unchanged when λ is increased (the amplitude becomes respectively 0.045 a.u. for $\lambda = 1$, 0.14 a.u. for $\lambda = 3$, and 0.16 a.u. when $\lambda \rightarrow \infty$).

In this series, the shape of all holes results mainly from angular correlation, which comes from mixing with the $2p$ orbital. Whereas the probability to find an electron with β spin on the same side of the nucleus as the reference electron with α spin is decreased, the probability of finding an electron with β spin on the opposite side is increased. The

amplitude of the $2p_x$ natural orbital is indeed close to its maximum in this region (cf., e.g., Fig. 1 in Ref. [33]). Thus, the excited configuration $2p^2$ is responsible for the angular correlation effects that are observed.

For the second series (when the reference electron is at 0.4 a.u. from the nucleus), the initial angular shape (for $\lambda = 0.1$, where the amplitude equals $4 \cdot 10^{-5}$ a.u.) is still observed (see Fig. 7).

But as λ is augmented, the shape of the hole is then modified by radial correlation (see Fig. 8 for $\lambda = 1$, where the amplitude equals 0.07 a.u.), to obtain a Coulomb hole where angular correlation is very weak (the contour plot however exhibits an asymmetrical shape).

For λ 's greater than 1, the shape basically remains unchanged (the amplitude becomes 0.35 a.u. for $\lambda = 3$ and 0.45 a.u. when $\lambda \rightarrow \infty$).

Thus, we observe that whatever the position of the reference electron may be, the shape of the correlation hole for weak interaction strengths is

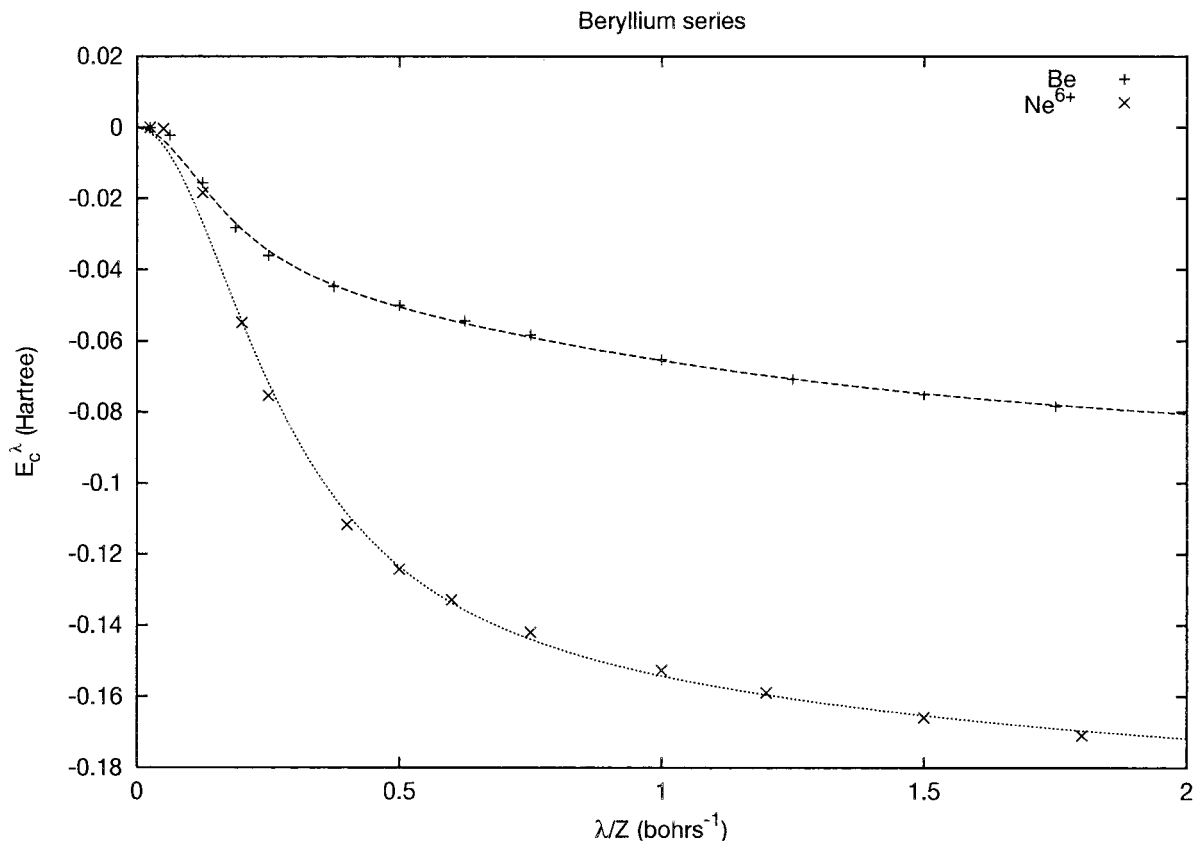


FIGURE 5. Fits of the λ -dependent correlation energies for systems belonging to the beryllium series (Be and Ne^{8+}) according to the fit function (17).

determined by angular correlation effects. To understand why, let us examine the third-order series of our modified two-electron operator near $\lambda = 0$,

$$\frac{\text{erf}(\lambda r_{12})}{r_{12}} \approx \frac{2\lambda}{\sqrt{\pi}} - \frac{2\lambda^3}{3\sqrt{\pi}} r_{12}^2 + \dots \quad (31)$$

We must then determine which bielectronic integrals contribute to the correlation energy. If the

TABLE III
Fitting parameters and root mean square (RMS) of the λ -dependent correlation energies according to the fit function (17).

Systems	RMS	α	β	γ
He	0.000107	0.11118	1.23083	0.00140
C^{4+}	0.000226	0.34688	1.53225	0.00093
Ne^{8+}	0.000101	0.24156	1.73407	0.00197
Be	0.001253	0.05138	1.58206	-0.07969
Ne^{6+}	0.003603	0.28233	3.73581	-0.58459

only virtual orbitals are $2s$ and $2p$, the integrals are $(1s2s|1s2s)$ and $(1s2p|1s2p)$ (in chemists' notation). The first term in the series is a constant, so that the corresponding integrals vanish because the atomic orbitals are orthonormal. The second term depends on the bielectronic operator $r_{12}^2 = r_1^2 + r_2^2 - 2\mathbf{r}_1 \cdot \mathbf{r}_2$. The first two operators are one-electronic so that both integrals still vanish. Only the last operator yields a nonzero contribution to the correlation energy. It is a product of two one-electronic operators so that we can split the two integrals. For symmetry reasons, the only nonzero integrals are of the type $\int 1s(r_i)x_i 2p_x(r_i) d r_i$. It is this peculiar type of integral that is responsible for all the angular effects when the interaction strength is weak, and no radial correlation effects exist.

Conclusion

Among all possible adiabatic connection paths that link the noninteracting reference system to the

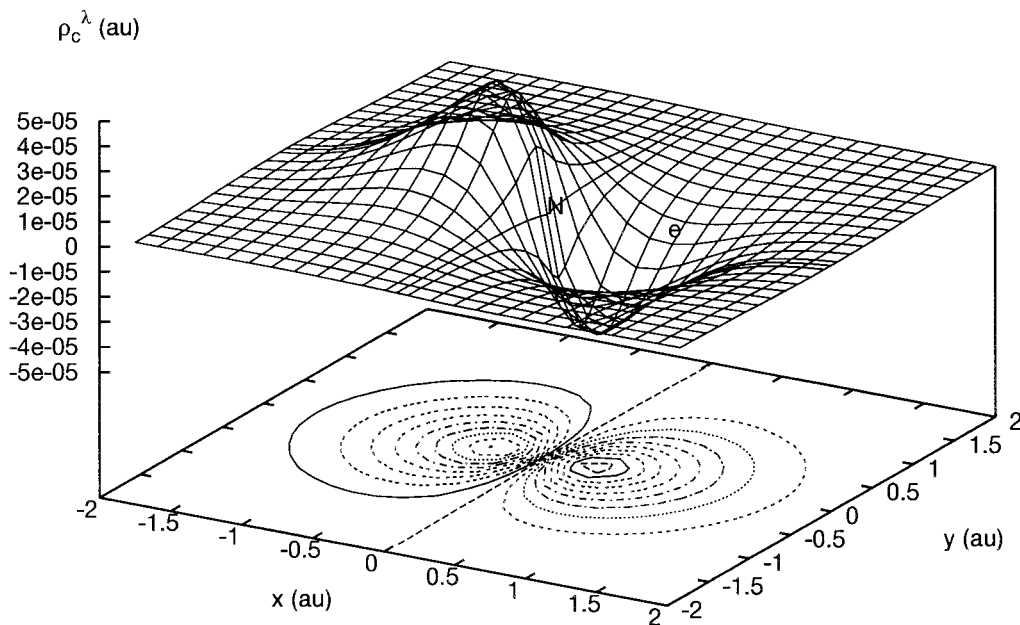


FIGURE 6. Correlation hole of He for $\lambda = 0.1$ when the reference electron is at position $x = 0.85$ a.u. and $y = 0.0$ a.u. On the surface plot, the N label represents the nucleus position, and the e label, the reference electron position.

physical one, a nonlinear one that involves the error function was studied. By searching for the universal functional defined by Lieb, that is by optimizing the local potential that is mapped with the physical electron density, we have calculated the exchange and correlation energies along that adiabatic con-

nection path for systems that belong to the helium and beryllium isoelectronic series. We have also computed the correlation holes of helium as the interaction strength increases and observed that angular correlation effects always prevail when this strength is weak. Such data should serve for the

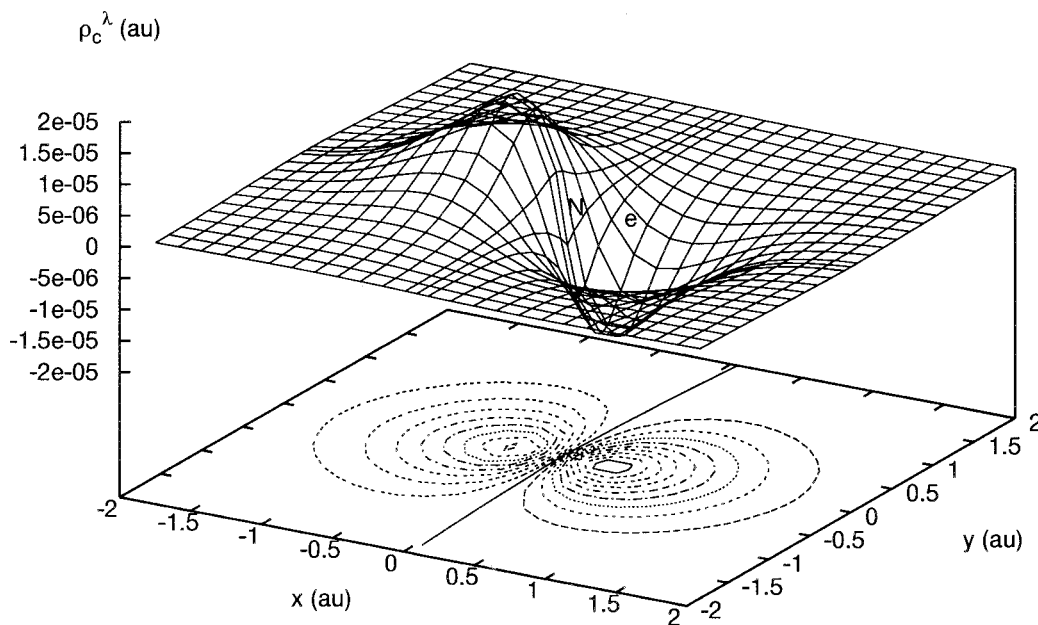


FIGURE 7. Correlation hole of He for $\lambda = 0.1$ when the reference electron is at position $x = 0.4$ a.u. and $y = 0.0$ a.u. On the surface plot, the N label represents the nucleus position, and the e label, the reference electron position.

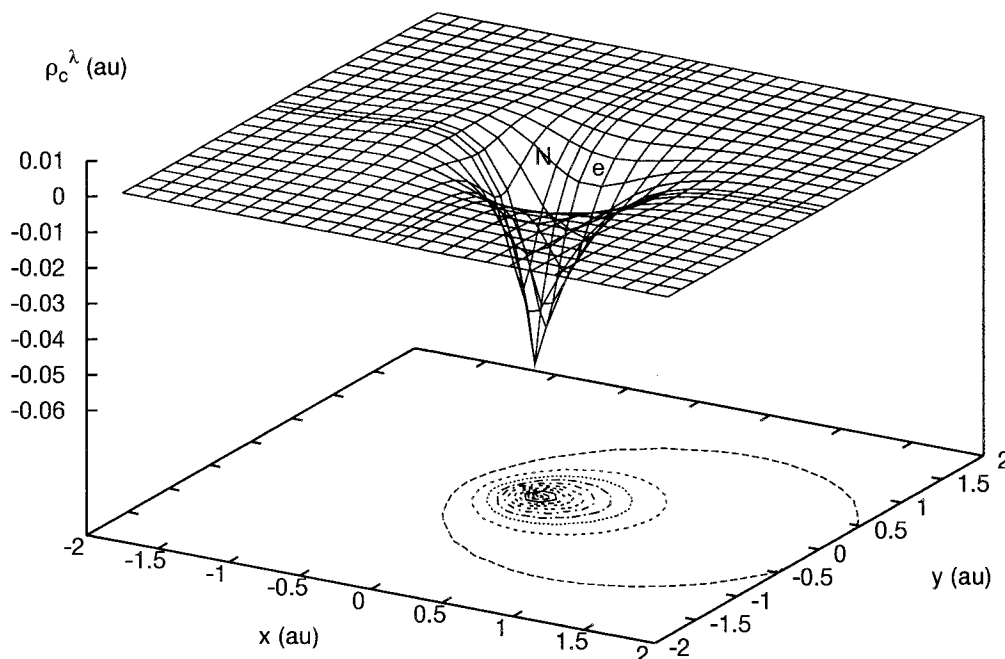


FIGURE 8. Correlation hole of He for $\lambda = 1.0$ when the reference electron is at position $x = 0.4$ a.u. and $y = 0.0$ a.u. On the surface plot, the N label represents the nucleus position, and the e label, the reference electron position.

improvement of current density functionals or for the design of new approximations.

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