Correlation energies for some two- and four-electron systems along the adiabatic connection in density functional theory

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Switching on the electron–electron interaction connects the Kohn–Sham to the physical system. The correlation energy, the only unknown energy component in this process, is determined at fixed density, using a technique based on the Lieb Legendre transform definition of the universal density functional. Results are shown for this adiabatic coupling process for He,Ne⁸⁺,Be,Ne⁶⁺ as well as for the exponential densities $n_{N,\zeta}(r) = N(\zeta^3/\pi)e^{-2\zeta r}$ (N=2 or 4; $\zeta \ge 1$; for N=4 degeneracy is present and ¹D and ³P are analyzed). The data are fitted to a rational approximant and appear to be in good agreement with those given by the less computationally demanding Harris–Jones adiabatic connection. © 1999 American Institute of Physics. [S0021-9606(99)30806-0]

I. INTRODUCTION

In order to get more insight into the nature of density functionals, the construction of the Kohn–Sham potential has received much attention. Little is known about the connection of the Kohn–Sham system with the physical system. This can be done by using the adiabatic connection procedure of Harris and Jones¹ (along which the density is only kept the same at the full interaction strength and for the noninteracting system), or by keeping the density constant along the whole path.^{2,3} Although the first way is certainly simpler to perform, the latter is closely related to the philosophy of density functionals.

In a previous paper⁴ we presented results for the Harris– Jones adiabatic connection in the He and Be series. Here we will show that these results differ little from those obtained by keeping the density constant as long as the interaction strength λ lies between 0 and 1. It is, however, of interest to consider the more strongly correlated systems, too, where the electron–electron interaction is enhanced ($\lambda > 1$) for which we will give results in a forthcoming paper.

We will also consider the system described by an exponential density, which by integration yields the number of electrons, N:

$$n_N(r) = \frac{N}{\pi} e^{-2r}.$$
(1)

Please notice, that if the density would be chosen to yield by integration one, all n_N would be transformed into the hydrogen density: The only difference produced by going from one n_N to another is due to the change in the number of electrons and not to a change of the shape of the density. Other densities

$$n_{N,\zeta}(r) = N \frac{\zeta^3}{\pi} e^{-2\zeta r}$$
(2)

are related to n_N by the scaling relation: $n_{N,\zeta}(r) = \zeta^3 n_N(\zeta r)$. Since the correlation energy functional is universal, it is important that it also treats correctly simple ex-

ponential densities which resemble the atomic densities. $n_{N,\zeta}$ generates a family of densities characterized by the parameters N and ζ . For a given N, we have just one parameter generating a series of density functional values, as we have for the uniform electron gas [where the single parameter is $r_s = (3/4\pi n)^{1/3}$]. The explicit dependence on N is also important. Thus, for N = 1 the correlation energy is trivially equal to zero.

Coordinate scaling is known to be closely related to the adiabatic connection (see, e.g., Ref. 5, and references therein). We will use the latter in order to generate the first.

Besides the purely academic interest in finding the connection between the real and the Kohn–Sham system, the adiabatic connection has been used in designing approximations to the exact density functionals (see, e.g., Ref. 6 or 7). In these papers the dependence of the energy on λ has some assumed form, satisfying certain physical constraints, and yields good correlation energies. It is thus of interest to accurately know the real dependence on λ . Hood *et al.*⁸ made a quantum Monte Carlo investigation for Si, where the potential keeping the density constant has been taken from the local density approximation. After completion of our work we learned that D. Joubert has also performed an adiabatic coupling calculation for the He series.⁹

II. METHOD

A. Definitions and properties

Lieb¹⁰ defined the universal Legendre transform functional F[n] of the electron density *n* as

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

where E[v] is the ground state energy for the system of $N = \int n$ interacting electrons in the external potential v.

We are interested in systems having fixed ground state density *n* at varying interaction strength λ , with Hamiltonian

$$\hat{H}^{\lambda} = \hat{T} + \lambda \hat{V}_{ee} + \hat{V}^{\lambda},$$

where \hat{T} is the operator for the kinetic energy, \hat{V}_{ee} that for the electron–electron interaction, and \hat{V}^{λ} that for the external local potential. Please notice that for $\lambda = 1$ we describe the physical interaction, for $\lambda = 0$ the Kohn–Sham noninteracting system and that for other λ , \hat{V}^{λ} is not known beforehand. To obtain the universal density functional at a given λ , $F^{\lambda}[n]$, we have to replace E[v] in Eq. (3) by that for the system in which the electron–electron interaction is modified by λ :

$$F^{\lambda}[n] = \max_{v} \mathscr{F}^{\lambda}[n;v], \qquad (4)$$

where

$$\mathscr{F}^{\lambda}[n;v] = E^{\lambda}[v] - \int nv \tag{5}$$

and $E^{\lambda}[v] = \min_{\Psi} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} + \hat{V} | \Psi \rangle$ with $\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i)$. If a maximizing potential v^{λ} exists, then according to Hohenberg and Kohn,¹¹ it is the one which has *n* as the ground state density:

$$F^{\lambda}[n] = E^{\lambda}[v^{\lambda}] - \int nv^{\lambda}, \qquad (6)$$

$$F^{\lambda}[n] = \langle \Psi^{\lambda} | \hat{T} + \lambda \hat{V}_{ee} | \Psi^{\lambda} \rangle, \qquad (7)$$

where Ψ^{λ} is the wave function minimizing $\langle \hat{H}^{\lambda} \rangle$ (i.e., $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$) and yielding the density *n*. For example, for $\lambda = 0$, $v^{\lambda=0}$ will be the Kohn–Sham potential; for $\lambda = 1$, $v^{\lambda=1}$ will be that corresponding to the physical system having the ground state density *n*. The Harris–Jones adiabatic connection¹ corresponds to approximating

$$v^{\lambda} \approx (1-\lambda)v^{\lambda=0} + \lambda v^{\lambda=1}.$$
(8)

We can define the correlation energy for interaction strength λ by

$$E_{c}^{\lambda} = \langle \Psi^{\lambda} | \hat{H}^{\lambda} | \Psi^{\lambda} \rangle - \langle \Psi^{\lambda=0} | \hat{H}^{\lambda} | \Psi^{\lambda=0} \rangle \tag{9}$$

or equivalently, when the density is kept fixed, by

$$E_{c}^{\lambda} = F^{\lambda}[n] - F^{\lambda=0}[n] - \lambda \langle \Psi^{\lambda=0} | \hat{V}_{ee} | \Psi^{\lambda=0} \rangle$$
(10)

$$= \langle \Psi^{\lambda} | \hat{T} + \lambda \hat{V}_{ee} | \Psi^{\lambda} \rangle - \langle \Psi^{\lambda=0} | \hat{T} + \lambda \hat{V}_{ee} | \Psi^{\lambda=0} \rangle.$$
(10a)

For $\lambda = 1$, Eqs. (9) and (10a) yield the usual density functional definition of the correlation energy.

We are also interested in obtaining the correlation energies of a family of exponential densities $n_{N,\zeta}$, Eq. (2). These can be related to the correlation energies of the systems with interaction strength $\lambda = 1/\zeta$ yielding the density n_N of Eq. (1) by using^{12,13}

$$E_{c}[n_{N,\zeta}] = \zeta^{2} E_{c}^{1/\zeta}[n_{N}].$$
(11)

An even more general form, also obtained from the previous scaling relationship is

$$E_c^{\lambda}[n_{N,\zeta}] = \zeta^2 E_c^{\lambda/\zeta}[n_N].$$
(12)

Thus, the results obtained for $n_{N,\zeta=1}=n_N$ for $0 \le \lambda \le 1$ can be used to get the correlation energies for systems with den-

sities $n_{N,\zeta}$ for $0 \le \lambda \le \zeta$. (For large ζ , our values can yield data for larger λ , but for $\zeta < 1$, $E_c^{\lambda=1} = E_c$ will not be obtained.)

B. Technical details

In practice v^{λ} is approximated by \tilde{v}^{λ} , Ψ^{λ} by $\tilde{\Psi}^{\lambda}$ yielding \tilde{n}^{λ} and thus $E[v^{\lambda}]$ by $\tilde{E}[\tilde{v}^{\lambda}]$. As we have noticed that computing E_c^{λ} from Eqs. (6) and (10)

$$\widetilde{E}_{v}^{\lambda} = \left(\widetilde{E}^{\lambda} [\widetilde{v}^{\lambda}] - \int n \widetilde{v}^{\lambda} \right) - \left(\widetilde{E}^{\lambda=0} [\widetilde{v}^{\lambda=0}] - \int n \widetilde{v}^{\lambda=0} \right) - \lambda \langle \widetilde{\Psi}_{n}^{\lambda=0} | \widehat{V}_{ee} | \widetilde{\Psi}_{n}^{\lambda=0} \rangle$$
(13)

is quite stable with respect to modifications of the potential, we will present the correlation energy computed according to that formula. Other possibilities to calculate E_c^{λ} are as follows:

(1) From Eq. (10a) $\widetilde{E}_{c_{a}}^{\lambda} = \langle \widetilde{\Psi}^{\lambda} | \widehat{T} + \lambda \widehat{V}_{ee} | \widetilde{\Psi}^{\lambda} \rangle - \langle \widetilde{\Psi}^{\lambda=0} | \widehat{T} + \lambda \widehat{V}_{ee} | \widetilde{\Psi}^{\lambda=0} \rangle.$ (2) From Eq. (9) $\widetilde{E}_{c_{b}}^{\lambda} = \langle \widetilde{\Psi}^{\lambda} | \widehat{T} + \widehat{\widetilde{V}}^{\lambda} + \lambda \widehat{V}_{ee} | \widetilde{\Psi}^{\lambda} \rangle$ $- \langle \widetilde{\Psi}^{\lambda=0} | \widehat{T} + \widehat{\widetilde{V}}^{\lambda} + \lambda \widehat{V}_{ee} | \widetilde{\Psi}^{\lambda=0} \rangle.$

The difference between \tilde{E}_c^{λ} , $\tilde{E}_{c_a}^{\lambda}$ and $\tilde{E}_{c_b}^{\lambda}$ disappears, of course, in an exact calculation (when $\tilde{n}^{\lambda} = n$), as can be easily seen from

$$\widetilde{E}_{c}^{\lambda} = \widetilde{E}_{c_{a}}^{\lambda} - \int \widetilde{v}^{\lambda} (\widetilde{n}^{\lambda} - n) - \int \widetilde{v}^{\lambda=0} (\widetilde{n}^{\lambda=0} - n)$$
$$= \widetilde{E}_{c_{b}}^{\lambda} - \int (\widetilde{v}^{\lambda} - \widetilde{v}^{\lambda=0}) (n - \widetilde{n}^{\lambda=0}).$$
(14)

E[v] is obtained by using the program MOLPRO.¹⁴ For He, Ne⁸⁺ and $n_{N=2,\zeta=1}$ full configuration interaction (CI) was used. For Be and Ne⁶⁺ single and double excitations with respect to a wave function obtained from a multiconfiguration self-consistent field calculation in the space of the first two s and the first set of p orbitals were considered. The case $n_{N=4, \zeta=1}$ is more complicated. It turns out that the ordering of the Kohn-Sham eigenstates is similar to that of the particle enclosed in a sphere of zero potential:¹⁵ $\epsilon(1s)$ $<\epsilon(2p)<\epsilon(2s)$ (see also Ref. 16). This corresponds to an open-shell ground state. The spherical density $n_{N=4,\zeta=1}$ can be obtained via an ensemble (cf. Ref. 17). [As we use Eq. (4) we do not have any problem treating ensemble densities to obtain the universal density functional.] Two electrons in the p shell generate the states ${}^{3}P$, ${}^{1}D$, and ${}^{1}S$. As the program MOLPRO does not explicitly treat spherical symmetry, a slight difference ($<10^{-4}$ hartrees) between D states may appear in the CI calculations with single and double excitations from the reference configurations in spite of the fact that the orbitals used are respecting the spherical symmetry.

Uncontracted even tempered Gaussian basis sets, up to f functions, were used in the calculations. For each angular quantum number, M exponents α_n were produced by the rule

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TABLE I. Even tempered Gaussian basis set exponents obtained from Eq. (15). *M* is the number of Gaussians, α_c the center, and δ the ratio of two consecutive exponents.

		s			р			d			f	
Functions System	М	α_c	δ	М	α_c	δ	М	α_c	δ	М	α_c	δ
He	21	2.1	40.0	7	2.1	3.0	5	2.1	3.0	3	2.1	3.0
Ne ⁸⁺	21	2.1	2030.0	7	2.1	100.0	5	2.1	100.0	3	2.1	100.0
$n_{N=2, \zeta=1}$	21	2.1	10.0	7	2.1	0.75	5	2.1	0.75	3	2.1	0.75
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
$n_{N=4, \zeta=1}$	21	2.1	10.0	14	1.8	0.35	5	2.3	1.025	3	2.4	1.025

$$\alpha_n = \alpha_c \, \delta^{(2n-M-1)/2}, \quad n = 1, ..., M.$$
 (15)

The central exponents α_c and the ratio δ can be found in Table I.

We will consider here a class of potentials v_{ps} easily generated by existing computer codes, where in order to treat pseudopotentials replacing the atomic cores, the following form is used:

$$v_{\rm ps}(r) = \sum_{i} C_{i} r^{p_{i}} \exp(-\gamma_{i} r^{2}) + \frac{C}{r}.$$
 (16)

r is the distance from the nucleus, p_i are integers larger than -2, γ_i is positive, *C* is given by the asymptotic conditions [cf. Eqs. (A1) and (A4) in the Appendix]; the parameters C_i , p_i , γ_i are obtained by maximizing $\mathscr{F}^{\lambda}[n, v_{ps}]$ [cf. Eq. (5)] with respect to v_{ps} : For a given number of terms, we try several powers p_i , and maximize by using the SIMPLEX procedure from Numerical Recipes.¹⁸ We repeat this procedure after modifying the values of the p_i and the number of terms. (Developing the potential in terms of basis functions is common also for obtaining Kohn–Sham potentials, see, e.g., Refs. 19 and 20, or in the practice of density functional calculations, see, e.g., Ref. 21.)

Although Eq. (4) is the only criterion used to obtain \tilde{v}^{λ} , during our optimization process, we also use as checks the following quantities which should be zero for the exact potentials:

$$\Delta_1 = \int \frac{(\tilde{n}^{\lambda} - n)}{r} d^3 r$$

related to the difference between the various definitions of \tilde{E}_{c}^{λ} [Eq. (14)];

$$\Delta_2 = \frac{1}{2} \int \frac{(\tilde{n}^{\lambda}(\mathbf{r}_1) - n(\mathbf{r}_1))(\tilde{n}^{\lambda}(\mathbf{r}_2) - n(\mathbf{r}_2))}{|\mathbf{r}_2 - \mathbf{r}_1|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

the criterion used, e.g., by Zhao and Parr [Eq. (43) of Ref. 22] for obtaining Kohn-Sham potentials;

$$\Delta_{3} = \tilde{E}^{\lambda} [\tilde{v}^{\lambda}] + \langle \Psi^{\lambda} | \hat{T} | \Psi^{\lambda} \rangle - \int \tilde{n}^{\lambda}(r) \tilde{v}^{\lambda}(r) d^{3}r$$
$$- \int n(r) \mathbf{r} \cdot \nabla \tilde{v}^{\lambda}(r) d^{3}r$$

derived from the virial relation [see, for instance, Eq. (9) of Ref. 17];

$$\Delta_4 = \left(\alpha - \sum_{i}^{p_i = -1} C_i\right)^2$$

[with $\alpha = \zeta$, cf. Eq. (2), or *Z*, the nuclear charge] is obtained for $v^{\lambda=0}$ from the asymptotic condition at $r \rightarrow 0$ [cf. Eq. (A6) in the Appendix].

As we are interested in calculating E_c^{λ} , the stationarity property of F[n] is convenient. The errors in computing $\mathscr{P}^{\lambda}[n,v]$ will be of second order in δv , while Δ_1 will be of first order. This justifies our preference for calculating the correlation energy according to Eq. (13). If we want, however, to meet all the criteria, the minimization is slowly converging: sometimes more than 5000 steps are necessary.

Although we are interested in obtaining only the correlation energy, we would like to point out some of the possible difficulties encountered if one would like to obtain v^{λ} . too. In fact, having numerically stable values for the correlation energies does not mean that we have generated unambiguously the corresponding v^{λ} , too. For example, it has been shown^{23,24} that a shift by a constant over the physically significant region of space will only negligibly affect the measures of similitude of the density produced. Of course, such a shift produces a shift in the total energy, too, but does not essentially affect the wave function obtained and thus the correlation energy. Another way to change the potential without affecting the density is to add a rapidly oscillating perturbing potential. A related problem was pointed out by Schipper et al.:²⁵ Gaussian basis sets yield oscillations in the potential; they noticed, however, that average values are stable.

As we use limited wave function basis sets, we cannot guarantee that our approximate F^{λ} is smaller than the exact one, in spite of our search of a maximizing $v_{ps} \approx v^{\lambda}$ [cf. Eqs. (4), (5), and (16)] our approximate $E^{\lambda}[v]$ might lay above the exact one. Thus, for v^{λ} , our limited basis set $\mathscr{F}^{\lambda}[n,v^{\lambda}]$ might get larger than the exact $F^{\lambda}[n]$. Searching for the maximizing potential in the limited basis set leads to an even larger value. In other words, the approximate F^{λ} lies below or above the exact value, according to the quality of the model potential or of the basis set used.

III. RESULTS

The correlation energies E_c^{λ} for N=2 (He, Ne⁸⁺, $n_{N=2,\zeta=1}$) and for N=4 (Be, Ne⁶⁺, and the two states ³P and ¹D of $n_{N=4,\zeta=1}$) are shown in Fig. 1. The curves for the



FIG. 1. Correlation energies E_c^{λ} , Eq. (13), in mhartree (a), and their derivatives, $V_c(\lambda) = \partial E_c^{\lambda} / \partial \lambda$, Eq. (19), in mhartree (b), as a function of the interaction strength λ . The curves can be attributed to the systems according to the values of $E_c^{\lambda} = 1$, which decreases in the following order: $n_{N=2,\zeta=1}$, He, Ne⁸⁺; $n_{N=4,\zeta=1}({}^{3}P)$, $n_{N=4,\zeta=1}({}^{1}D)$, Be, Ne⁶⁺.

two-electron systems are very close, as are those for Be and $n_{N=4,\zeta=1}$. Strong correlation effects greatly lower the curve of Ne⁶⁺. We will tabulate here only some of the results, due to the large amount of data. Further results are available either on request or on our web-site.²⁶ Data for $\lambda = 0$ and for $\lambda = 1$ are given in Tables II and III, respectively.

Here are some considerations about the accuracy of our results. For the Kohn–Sham system ($\lambda = 0$) it turns out that our values for He and Ne⁸⁺ agree within 1 mhartree with the more accurate values given by Umrigar and Gonze.²⁷ For Be the comparison is less favorable for the noninteracting kinetic energy, and the average energy of the interaction with the external potential obtained from our density, where the differences to more accurate quantum Monte Carlo results²⁸ are of a few mhartree. We find, however, a better agreement (within 1 mhartree) when comparing the electron-electron interaction, and its components. For $\lambda = 1$ we can compare our correlation energies with those of Refs. 27 and 28. Again, for He and Ne^{8+} we get a good agreement (within 1 mhartree). For Be, however, the error is larger (3 mhartrees). We can also compare our CI energies with the "exact" ones of Refs. 29 and 30. For He and Ne^{8+} our energies are 1 mhartree above the exact ones, while for Be and Ne⁶⁺ our values are again 3 mhartrees too high. It thus seems that the significantly lower value for the density functional definition of the correlation energy (-0.189 hartree) than the difference between the CI and Hartree–Fock values (-0.177 hartree) will be also present in more accurate calculations. The existence of such an increase has been noticed by Huang and Umrigar³¹ and also appears in the calculations done by nonuniform scaling transformations in the Be series.³²

Instead of tabulating our results for intermediate λ , we give a least-squares fit with a rational approximant³³ to the correlation energies E_c^{λ} for $0 < \lambda < 1$ (cf. the ansatz made in Ref. 34):

$$E_c^{\lambda} \approx \frac{a\lambda^2}{1+b\lambda}.$$
(17)

The parameters *a* and *b* are given in Table IV. The maximal errors of the fit are of 10^{-6} hartree for N=2, but are larger by one to two orders of magnitude for N=4. While this accuracy seems remarkable, we would like to point out that errors can propagate when scaling the density [Eq. (11)] due to the factor ζ^2 . For example, the error obtained in the fit of $E_c^{\lambda=1/10}[n_{N,\zeta=1}]$ will be multiplied by a factor of 100 when computing $E_c[n_{N,\zeta=10}]$. In order to get an idea about the effect of the fit, we can also use our ansatz and set of λ points to fit the correlation energy of the uniform electron gas with density given by $r_s=1$, by using the following relationship:

$$\boldsymbol{\epsilon}_{c}^{\boldsymbol{\Lambda}}(\boldsymbol{r}_{s}) = \boldsymbol{\lambda}^{2} \boldsymbol{\epsilon}_{c}(\boldsymbol{\lambda}\boldsymbol{r}_{s}),$$

where ϵ_c is the correlation energy per particle. We thus know that for $\lambda \rightarrow 0$ we should have a $\lambda^2 \ln(\lambda)$ dependence (in the uniform electron gas), which is not satisfied by our approximation. For large λ , the ansatz is capable of reproducing the correct λ dependence. This cannot be expected to occur, however, if we try to reproduce $\epsilon_c^{\lambda}(r_s=1)$, with λ lying between 0 and 1. In this case we obtain a=-0.1099, b= 0.8433 and a maximal error of 4×10^{-4} . We can now use this fit to obtain ϵ_c at different r_s . We get: $\epsilon_c(r_s=0.1)$ ≈ -0.101 hartree (instead of -0.121) and $\epsilon_c(r_s=10)$ ≈ -0.012 hartree (instead of -0.019).

The fit can be improved, however, by choosing a more flexible ansatz:

TABLE II. Results at $\lambda = 0$, in hartree. $E_{\rm KS} = T_s + V_{\rm KS}$: Kohn–Sham energy; $T_s = \langle \tilde{\Psi}^{\lambda=0} | \hat{T} | \tilde{\Psi}^{\lambda=0} \rangle$: noninteracting kinetic energy; $V_{\rm KS} = \langle \tilde{\Psi}^{\lambda=0} | \hat{V}^{\lambda=0} | \tilde{\Psi}^{\lambda=0} \rangle$: interaction with Kohn–Sham potential; $F^{\lambda=0} = E_{\rm KS} - \int n \hat{v}^{\lambda=0}$: Lieb density functional for the noninteracting system; $U = 1/2 \int \tilde{n}^{\lambda=0} \tilde{n}^{\lambda=0}/r_{12}$: Coulomb electron–electron interactions, $V_{\rm ee} = \langle \tilde{\Psi}^{\lambda=1} | 1/r_{12} | \tilde{\Psi}^{\lambda=1} \rangle$; $E_x = V_{\rm ee} - U$: exchange energy. $\tilde{\Psi}^{\lambda=0}$ is our approximation to the Kohn–Sham wave function (it yields $\tilde{n}^{\lambda=0} \approx n$).

System	$E_{\rm KS}$	T_s	V _{KS}	$F^{\lambda=0}$	U	$V_{\rm ee}$	E_x
Не	-1.807	2.867	-4.674	2.867	2.049	1.024	-1.024
Ne ⁸⁺	-87.816	93.863	-181.678	93.862	12.055	6.028	-6.028
$n_{N=2, \zeta=1}$	-1.000	1.000	-2.000	1.000	1.250	0.625	-0.625
Be	-9.136	14.588	-23.724	14.588	7.217	4.544	-2.673
Ne ⁶⁺	-95.562	110.154	-205.717	110.155	21.742	14.142	-7.600
$n_{N=4, \zeta=1}{}^{3}P$	-4.060	3.478	-7.539	3.478	5.000	3.426	-1.573
$n_{N=4, \zeta=1}$ ¹ D^{a}	-4.060	3.478	-7.539	3.478	5.000	3.481	-1.519

^aThe values given were obtained using the \hat{S}^2 eigenfunction.

$$E_c^{gl} \approx \frac{a\lambda^2}{1 + c\sqrt{\lambda} + b\lambda}.$$
(18)

Applying this to the uniform electron gas with $r_s = 1$, we get: a = -0.2051, b = 0.2240, c = 2.1912, with a maximal error of 2×10^{-5} . With this new fit, the errors for $r_s = 0.1$ and r_s = 10 are much smaller (≈ 1 mhartree), as we get for ϵ_c -0.120, and -0.020, respectively.

As the errors are larger for the fit of the correlation energies in the Be series, we re-did the fits for these systems using the more refined ansatz, Eq. (18). For Be we get a = -0.1284, b = 0.2779, and c = 0.1055 reducing the maximal error by an order of magnitude to 2×10^{-5} , and for Ne⁶⁺ by a factor of 4 to 10^{-4} (a = -0.3204, b = 0.3895, c = 0.3052). This fit does not improve the asymptotic $\lambda \rightarrow \infty$ value, as can be seen from the comparison of our a/b values with the "exact" $\lim_{\lambda\to\infty} E_c^{\lambda}/\lambda$ given by Seidl *et al.*³⁵ (-0.4754, -2.7675, for He and Ne⁸⁺, respectively). As we used for the fits values for λ lying between 0 and 1, we expect the limit $\lambda \rightarrow 0$ to be better described. This can be confirmed by comparing our values of a for N=2 (cf. Table IV) with -0.0467, the "exact" value reported by Ivanov and Levy^{36,37} for the exponential density.

Applying the scaling relationship, Eq. (12), to the fit, [Eq. (17)], we see that for the density $n_{N,\zeta}$, *a* will be independent of ζ , while $b=b(\zeta)=b(\zeta=1)/\zeta$. This means that for large ζ , the correlation energy at $\lambda = 1$ is essentially given

by the second-order expression $E_c \approx a\lambda^2$. For decreasing ζ , E_c is more and more dominated by the linear behavior given by the asymptote $\lambda \rightarrow \infty$ describing the hypercorrelated case. In the He series, we have the same qualitative behavior as for $n_{N,\zeta}$. The *a* coefficients are nearly the same for all N=2systems studied here (cf. Table IV). The coefficient b is 5.6 times smaller for Ne⁸⁺ than for He which is in accordance with estimates we can get from the behavior of the density near the nucleus (the ratio of the nuclear charges is 5) and in the tail region (the ratio of the square roots of the ionization potentials is 7.0^{38}). The behavior in the Be series is, however, significantly different. We see that for Ne⁶⁺ the coefficient *a* is different from that of Be, and that *b* is smaller for the latter. The large b coefficients indicate a significant difference between the second-order and exact correlation energies, which is usually attributed to near degeneracy.

The E_c^{λ} curve for the $n_{N=4,\zeta=1}$ ³*P* state lies above that of the ¹*D* state. As at $\lambda = 0$ the two states are degenerate, and at first-order perturbation theory, the ³*P* state is below the ¹*D* state (Hund's rule), we expect that after a certain λ , correlation will start to dominate, and the energy of the ¹*D* state will lie below that of the ³*P* state. Using Eq. (11) this means that for large ζ the ground state is ³*P*, while for small ζ it is the ¹*D* state. In the latter case, a change of the nature of the ground state occurs along the adiabatic coupling process.

From the variational principle and the Hellmann– Feynman theorem one obtains that the first two derivatives of

TABLE III. Results at $\lambda = 1$, in hartree. $E_{\text{CI}} = \text{configuration interaction energy}; T = \langle \Psi^{\lambda=1} | \hat{T} | \Psi^{\lambda=1} \rangle$: interacting kinetic energy; $V = \langle \Psi^{\lambda=1} | \hat{V} | \Psi^{\lambda=1} \rangle$: interacting external potential energy; $F^{\lambda=1} = E_{\text{CI}} - \int n \tilde{v}^{\lambda=1}$: Lieb density functional of the interacting system; $E_{\text{HF}} = \text{Hartree-Fock energy}; V_{ee} = \langle \Psi^{\lambda=0} | 1/r_{12} | \Psi^{\lambda=0} \rangle; E_c = F^{\lambda=1} - F^{\lambda=0} - \langle \Psi^{\lambda=0} | V_{ee} | \Psi^{\lambda=0} \rangle; F^{\lambda=0}$ and $\langle \Psi^{\lambda=0} | V_{ee} | \Psi^{\lambda=0} \rangle$ are given in Table II.

System	$E_{\rm CI}$	Т	V	$F^{\lambda=1}$	$E_{\rm HF}$	$V_{\rm ee}$	E _c
Не	-2.903	2.903	-6.753	3.850	-2.862	0.946	-0.042
Ne ⁸⁺	-93.906	93.906	-193.751	99.845	-93.861	5.939	-0.045
$n_{N=2, \zeta=1}$	-1.668	1.030	-3.256	1.588	-1.631	0.557	-0.037
Be	-14.664	14.659	-33.703	19.039	-14.573	4.380	-0.093
Ne ⁶⁺	-110.288	110.286	-234.396	124.109	-110.111	13.822	-0.189
$n_{N=4, \zeta=1}{}^{3}P$	-7.869	3.540	-14.696	6.827	-7.794	3.287	-0.077
$n_{N=4, \zeta=1} {}^{1}D^{a}$	-7.959	3.550	-14.828	6.869	-7.871	3.319	-0.090

^aThe values given were obtained using the \hat{S}^2 eigenfunction.

TABLE IV. Fitting parameters *a* and *b*, in atomic units, for the approximate form, Eq. (17), for E_c^{λ} , Eq. (9), for the fixed density and the Harris–Jones adiabatic connection ($0 \le \lambda \le 1$).

	n fix	ed	Harris–Jones			
System	а	b	а	b		
Не	-0.0475	0.1414	-0.0475	0.1405		
Ne ⁸⁺	-0.0460	0.0253	-0.0460	0.0253		
$n_{N=2, \ \zeta=1}$	-0.0457	0.2270	-0.0457	0.2275		
Be	-0.1231	0.3269	-0.1235	0.3319		
Ne ⁶⁺	-0.2852	0.5108	-0.2857	0.5138		
$n_{N=4, \ell=1}{}^{3}P$	-0.0945	0.2205	-0.0946	0.2218		
$n_{N=4, \zeta=1}$ ¹ D	-0.1114	0.2335	-0.1126	0.2483		

 E_c^{λ} with respect to λ are nonpositive [cf. Eq. (65) in Ref. 39]. It is sometimes assumed that the third derivative is positive (see, e.g., Ref. 7). If the fit of Eq. (17) were exact, this property would hold in all the cases studied.

We analyzed the Harris–Jones adiabatic coupling [Eq. (8)] in a previous paper.⁴ It turns out that the E_c^{λ} obtained within this procedure is remarkably close (for the systems studied) to those obtained by keeping the density fixed for $0 < \lambda < 1$. This behavior might be understood by remembering that the constant-density and Harris–Jones E_c^{λ} coincide at $\lambda = 0$ and $\lambda = 1$. At these points, as the density obtained in Harris–Jones equals the exact one, and as^{4,39}

$$\frac{\partial E_{c}^{\lambda}}{\partial \lambda} = \langle \Psi^{\lambda} | \hat{V}_{ee} | \Psi^{\lambda} \rangle - \langle \Psi^{\lambda=0} | \hat{V}_{ee} | \Psi^{\lambda=0} \rangle, \qquad (19)$$

$$\frac{\partial E_{c,HJ}^{\lambda}}{\partial \lambda} = \langle \Psi_{HJ}^{\lambda} | \hat{V}_{ee} | \Psi_{HJ}^{\lambda} \rangle - \langle \Psi^{\lambda=0} | \hat{V}_{ee} | \Psi^{\lambda=0} \rangle + \int (n_{HJ}^{\lambda} - n) (v^{\lambda=1} - v^{\lambda=0}),$$

the first derivatives are the same. Finally, we know that the Harris–Jones correlation energy can never be higher than the one obtained by keeping the density constant, as $\mathscr{F}^{\lambda}[n, v_{\text{HJ}}^{\lambda}] \leq F^{\lambda}[n]$, cf. Eq. (3).⁴ Using the type of fit given in Eq. (17) we obtain the parameters given in Table IV. Taking into account that $v^{\lambda=1}$ is in general known and of the progress made in the last several years in computing $v^{\lambda=0}$, Eq. (8) seems to be a useful alternative to obtain approximations to v^{λ} .

In order to see the effect of assuming the λ dependence in the local density (LDA) and the generalized gradient (GGA) approximations,⁴⁰ we calculated ϵ_c^{λ} in these approximations by using the following relationship:^{12,13}

$$E_c^{\lambda} = \lambda^2 E_c[n_{1/\lambda}].$$

We then fitted the results by using the rational approximant, Eq. (17). The errors are quite large when fitting the LDA values (of the order of 0.001); the GGA errors are of the same order of magnitude as those of the accurate ϵ_c^{λ} . The resulting coefficients *a* and *b* are given in Table V. While the GGAs are in general close to the coefficients of the accurate fit, the LDA values are always larger. The exception appears in the Be series. The *a* coefficient is too small in Ne⁶⁺ by a factor of 2.6, and the *b* coefficient decreases strongly with

TABLE V. Fitting parameters *a* and *b*, in atomic units, to the local density (LDA) and to the generalized gradient approximation (GGA) correlation energies $(0 \le \lambda \le 1)$.

	LD.	A	GG	А
System	а	b	а	b
He Ne ⁸⁺ Be Ne ⁶⁺ $n_{N=4, \zeta=1}$ ¹ D	$\begin{array}{r} -0.2100 \\ -0.3031 \\ -0.1898 \\ -0.4130 \\ -0.5326 \\ -0.4012 \end{array}$	0.8752 0.5007 1.0801 0.8411 0.5957 0.9887	$\begin{array}{r} -0.0461 \\ -0.0479 \\ -0.0506 \\ -0.1045 \\ -0.1111 \\ -0.1376 \end{array}$	0.1003 0.0000 0.2183 0.2143 0.0751 0.2548

respect to Be instead of increasing. Due to the accuracy of the Harris–Jones approximation, we do not further pursue here the comparison of accurate with approximate density correlation energy functionals, but refer for more details to our previous publication.⁴

Very often, in order to get approximations to density functionals, the integrand in the coupling constant formula, $\partial E_c^{\lambda}/\partial \lambda$, Eq. (19), is used. As it can be obtained by taking the derivatives with respect to λ in Eqs. (17) or (18) and the numerical accuracy of E_c^{λ} seems better, we prefer the values obtained by fitting E_c^{λ} . For completeness, the values obtained by fitting the parameters *a* and *b* so that

$$\frac{d}{d\lambda}\frac{a\lambda^2}{(1+b\lambda)} = \frac{a\lambda(2+b\lambda)}{(1+b\lambda)^2}$$
(20)

follows our computed values of

$$V_{c}^{\lambda} = \langle \tilde{\Psi}^{\lambda} | \hat{V}_{ee} | \tilde{\Psi}^{\lambda} \rangle - \langle \tilde{\Psi}^{\lambda=0} | \hat{V}_{ee} | \tilde{\Psi}^{\lambda=0} \rangle, \qquad (21)$$

which are given in Table VI.

IV. CONCLUSIONS

We presented changes in the correlation energy produced by multiplying the electron–electron interaction by a factor λ (between 0 and 1) at fixed density for He,Ne⁸⁺,Be,Ne⁶⁺ as well as for the exponential densities $n_{N,\zeta}$, [Eq. (2), N=2 or N=4, $\zeta \ge 1$]. Although apparently similar to atomic densities, the $n_{N=4,\zeta}$ correlation energy behaves differently from the Be-series systems, while the $n_{N=2,\zeta}$ resemble the He series. The data could be fitted rea-

TABLE VI. Fitting parameters *a* and *b*, in atomic units, for the approximate form, Eq. (20), for the derivative of the correlation energy with respect to λ , Eq. (19), for the fixed density and the Harris–Jones adiabatic connection $(0 \leq \lambda \leq 1)$.

<i>b</i> 75 0.14	a	<i>b</i>
.14	-0.0476	0.1420
4590.024560.222210.313130.480470.22	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{c} 0.1420\\ 0.0236\\ 0.2270\\ 0.3203\\ 0.4920\\ 0.2263\end{array}$
	.59 0.02 .56 0.22 .21 0.31 .13 0.48 .47 0.22 .15 0.23	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

sonably well to a simple rational approximant [Eq. (17) and Table IV]. One can notice the agreement with data obtained when making the Harris–Jones adiabatic connection [cf. Eq. (8)] is very good.

It is our hope that our results can be used:

- as benchmarks for studying the behavior of density functionals,
- (2) for obtaining better density functionals, as we now have provided numerically the λ dependency of the correlation energy (the other parts of the energy have a trivial λ dependency);
- (3) for alternative approximations to the exact correlation energy (in a way similar to the case of the uniform electron gas) by using the results for the exponential density for different N and ζ.

Finally we would like to point out that the procedure used in this paper, based upon the Lieb definition of the universal density functional, although computationally demanding, can be easily used by anyone possessing an *ab initio* code treating pseudopotentials and calculating correlation energies.

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APPENDIX: ASYMPTOTIC PROPERTIES USED FOR CONSTRUCTING THE POTENTIAL V^{λ}

As we try to obtain v^{λ} via Eq. (4), without knowing its form, it is helpful to have some information about its properties, e.g., its behavior at large *r*. Asymptotically, for a Coulomb external potential -Z/r, the Kohn–Sham potential behaves like⁴¹

$$v^{\lambda=0} \rightarrow \frac{-Z+N-1}{r} \quad (r \rightarrow \infty).$$
 (A1)

We can repeat the arguments used to derive this equation for the exponential density $n_{N,\zeta}$. Asymptotically, the radial part of the highest occupied Kohn–Sham orbital will be proportional to $\sqrt{n_{N,\zeta}}$, i.e., to $e^{-\zeta r}$. Introducing it into the radial Kohn–Sham equation:

$$\left\{-\frac{1}{2}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{l(l+1)}{r^2}\right)+v_{n_{N,\zeta}}^{\lambda=0}(r)-\epsilon_i\right\}\varphi_i=0,\tag{A2}$$



FIG. 2. The potentials (multiplied by *r*) for the exponential densities $n_{N;\xi=1}$ (N=2: the dashed curve, N=4: the three solid curves). The horizontal line at $rv^{\lambda=0}=-1$, corresponding to the Kohn–Sham potential for N=2, is not shown. For N=4, the curve $rv^{\lambda=0}$ is above the two nearly superimposed curves of $rv^{\lambda=1}$ (¹D and ³P).

$$-\frac{\zeta^2}{2} + \frac{\zeta}{r} + \frac{l(l+1)}{2r^2} + v_{n_{N,\zeta}}^{\lambda=0}(r) - \epsilon_i = 0,$$
(A3)

which implies that, up to a constant, for large r:

$$v_{n_{N,\zeta}}^{\lambda=0}(r) \to -\frac{\zeta}{r} \quad (r \to \infty).$$
(A4)

In order to determine the behavior of $v^{\lambda=1}(r)$ for an exponential density $n_{N,\zeta}$ at large *r*, one can use the relationship between $v^{\lambda=1}(r)$ and $v^{\lambda=0}_{n_{N,\zeta}}(r)$,

$$v_{n_{N,\zeta}}^{\lambda=0}(r) = v_{n_{N,\zeta}}^{\lambda=1}(r) + v_{h}(r) + v_{xc}(r),$$

where v_h is the Hartree potential, and v_{xc} the exchangecorrelation potential. It is known that (see, e.g., Ref. 41)

$$v_h(r) \rightarrow \frac{N}{r} \quad (r \rightarrow \infty),$$

 $v_{xc}(r) \rightarrow -\frac{1}{r} \quad (r \rightarrow \infty)$

Therefore:

$$v_{n_{N,\zeta}}^{\lambda=1}(r) \rightarrow -\frac{\zeta+N-1}{r} \quad (r \rightarrow \infty).$$

We can extend this approach to obtain the asymptotic behavior for any λ . As the exchange–correlation potential is dominated by its exchange part, and the latter changes as linearly with λ , as does the Hartree potential, we obtain:

$$v_{n_{N,\zeta}}^{\lambda}(r) \to -\frac{\zeta}{r} - \lambda \frac{N-1}{r} \quad (r \to \infty).$$
 (A5)

Let us now consider the case $r \rightarrow 0$. For atoms, we know that the Hartree and the exchange–correlation potentials will go to a constant,⁴² as $r \rightarrow 0$. Thus, in this limit, the only diver-

gence in $v^{\lambda=0}$ is coming from the external potential. For the exponential density, both for $n_{N=2,\zeta}$ and $n_{N=4,\zeta}$ only the 1*s* orbital contributes to the density at the origin, and thus ϕ_{1s} is proportional to $\exp(-\zeta r)$. From Eq. (A2) one gets

$$v^{\lambda=0}(r) \rightarrow -\frac{\alpha}{r} \quad (r \rightarrow 0)$$
 (A6)

up to an arbitrary constant; α can be either equal to Z (atoms) or ζ (exponential density).

As the potentials for the exponential densities are new, we present them, after multiplication with *r*, for $\lambda = 0$ and $\lambda = 1$ in Fig. 2.

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