PHYSICAL REVIEW A VOLUME 43, NUMBER 3 1 FEBRUARY 1991

Density-driven self-consistent-field method: Density-constrained correlation energies in the helium series

Jerzy Cioslowski
Department of Chemistry and Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306-3006

(Received 4 June 1990)

The electron-correlation energies, calculated with the wave functions constrained to the Hartree-Fock density, are computed for the helium series and are compared with the exact (unconstrained) correlation energies. Imposition of the density constraints increases the energies by a surprisingly small amount. Both the $l=0$ (s) and $l=1$ (p) limit differences between the constrained and exact energies are demonstrated to scale like the reciprocal of the square of the atomic numbers. The computational results are rationalized by introducing rigorous definitions of the dynamical and nondynamical correlation energies.

INTRODUCTION

Due to the fact that, except for trivial cases, the exact ground-state solutions of the electronic Hamiltonian cannot be obtained by analytical methods, the Hartree-Fock (HF) approximation dominates modern electronic structure calculations. Solving the self-consistent-field equations yields the Hartree-Fock energy E_{HF} together with the Hartree-Fock spin orbitals that can be used for computing the HF electron density $\rho_{\mathrm{HF}} \equiv \rho_{\mathrm{HF}}(\mathbf{r})$. The exact ground-state energy E_{FCI} and the corresponding electron density $\rho_{\mathrm{FCI}} \equiv \rho_{\mathrm{FCI}}(\mathbf{r})$ may be obtained, in principle[1] within the full-configuration-interaction (FCI) method,[2] provided a complete (infinite) set of one-electron basis functions is used.

The celebrated theorem of Hohenberg and Kohn,[3] together with the constrained-search technique of Levy,[4] demonstrate existence (for a given external potential) of a density functional $E_{\mathrm{FCI}}[\rho]$, such that

$$E_{\mathrm{FCI}}[\rho_{\mathrm{FCI}}]=E_{\mathrm{FCI}} \leq E_{\mathrm{FCI}}[\rho] \ , \tag{1}$$

for any non-negative density ρ that integrates to the same number of electrons, N, as ρ_{FCI}. The functional $E_{\mathrm{FCI}}[\rho]$ is defined as follows: Given a set of one-electron functions (spin orbitals), a Hilbert space $\mathcal{H}_1$ is defined. Let $\mathcal{H}_N$ be the Hilbert space spanned by all N-electron antisymmetrized products of the one-electron functions and $\mathcal{P}$ be the subset of $\mathcal{H}_N$ consisting of those functions that yield ρ. Then $E_{\mathrm{FCI}}[\rho]$ is the minimum of the expectation value of the Hamiltonian for functions in $\mathcal{P}$. One should note that, for a finite-dimensional $\mathcal{H}_1$ which is used in practical calculations, care must be taken to guarantee that $\mathcal{P}$ is not empty. For an infinite-dimensional $\mathcal{H}_1$, $E_{\mathrm{FCI}}[\rho]$ coincides with the exact functional for the ground-state energy. Similarly, the existence of the density functional for the HF energy $E_{\mathrm{HF}}[\rho]$, with the property

$$E_{\mathrm{HF}}[\rho_{\mathrm{HF}}]=E_{\mathrm{HF}} \leq E_{\mathrm{HF}}[\rho] \tag{2}$$

for any non-negative density ρ that integrates to the same number of electrons as ρ_{HF}, can be demonstrated[4,5] and the functional can be written in an algebraic form.[6]

The difference between the HF and the FCI energy is traditionally called the electron-correlation energy.[7] It can be proven that the exact correlation energy is a functional of the HF density.[8] The same is true for the correlation energies calculated within various approximate methods.[9] One quickly realizes that properties of these functionals are closely related to those of $E_{\mathrm{HF}}[\rho]$ and $E_{\mathrm{FCI}}[\rho]$.

In this paper we attempt to shed more light on the structure of the density functional for the exact energy $E_{\mathrm{FCI}}[\rho]$. Due to its complexity, this cannot be accomplished by analytical methods even for simplest Coulombic systems. For this reason, one has to resort to numerical methods to compute the values of $E_{\mathrm{FCI}}[\rho]$ for different densities. The values of $E_{\mathrm{FCI}}[\rho]$ coming from the exact density of the ground state, ρ_{FCI}, and from the Hartree-Fock density ρ_{HF} are of particular interest. The former one is easily calculated using the standard FCI approach. To compute the latter one, we propose a density-constrained full-configuration-interaction procedure (DCFCI). This enables us to evaluate the electron-correlation energy at the HF electron density, which is defined as

$$e_{\mathrm{DCFCI}}=E_{\mathrm{DCFCI}}-E_{\mathrm{HF}}[\rho_{\mathrm{HF}}], \quad E_{\mathrm{DCFCI}}=E_{\mathrm{FCI}}[\rho_{\mathrm{HF}}] \ , \tag{3a}$$

whereas the exact correlation energy is given, as usual, by

$$e_{\mathrm{FCI}}=E_{\mathrm{FCI}}[\rho_{\mathrm{FCI}}]-E_{\mathrm{HF}}[\rho_{\mathrm{HF}}] \ . \tag{3b}$$

As we demonstrate in the Discussion section of this paper, the values of e_{DCFCI} and e_{FCI} make rigorous definitions of the dynamical and nondynamical correlation energies possible. To illustrate our method, we report the results of FCI and DCFCI calculations on the correlation energies in the helium series. Analogous calculations for more complicated systems are feasible, although they would be computationally more expensive. The same is true about calculations without the "frozen density" approximation (see below).

DENSITY-CONSTRAINED FULL-CONFIGURATION-INTERACTION METHOD

The exact energy of any system that is described by an electronic Hamiltonian can be in principle obtained through the FCI method and is given by

$$E_{\mathrm{FCI}}=\sum_{i,j}\Gamma_{ij}\langle\psi_i|\hat{T}+\hat{V}|\psi_j\rangle+\tfrac{1}{2}\sum_{i,j,k,l}\Gamma_{ijkl}\langle\psi_i\psi_j|r_{12}^{-1}|\psi_k\psi_l\rangle\ , \tag{4}$$

where $\hat{T}$ and $\hat{V}$ are the kinetic-energy and the nuclear attraction operators, and $\psi_i\equiv\psi_i(\mathbf{r})$ are orthonormal basis functions. These functions may or may not be identical with the Hartree-Fock spin orbitals. The first- and second-order density matrices Γ_{ij} and Γ_{ijkl} result from diagonalization of the FCI Hamiltonian matrix. The exact electron density is given by

$$\rho_{\mathrm{FCI}}(\mathbf{r})=\sum_{i,j}\Gamma_{ij}\psi_i^*(\mathbf{r})\psi_j(\mathbf{r}) \tag{5}$$

and is, in general, different from the HF density, $\rho_{\mathrm{HF}}(\mathbf{r})$. In this and the following equations we assume that the summation over the spin variable is carried out.

It is possible to define a new set of orthonormal basis functions, $\phi_i\equiv\phi_i(\mathbf{r})$, such that

$$\rho_{\mathrm{HF}}(\mathbf{r})=\sum_{i,j}\Gamma_{ij}\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\ . \tag{6}$$

The new functions are related to the old set by a nonlinear transformation[10]

$$\phi_i(\mathbf{r})=[\rho_{\mathrm{HF}}(\mathbf{r})/\beta(\mathbf{r})]^{1/2}\sum_j(S^{-1/2})_{ij}^*\psi_j(\mathbf{r})\ , \tag{7}$$

where

$$\beta(\mathbf{r})=\sum_{i,j}(S^{*-1/2}\Gamma S^{*-1/2})_{ij}\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\ . \tag{8}$$

The Hermitian generalized overlap matrix, $\mathbf{S}$,[11] is a solution of the equation

$$S_{ij}=\int[\rho_{\mathrm{HF}}(\mathbf{r})/\beta(\mathbf{r})]\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r}\ . \tag{9}$$

This equation has to be solved iteratively.

The energy

$$E_{\mathrm{DCFCI}}=\sum_{i,j}\Gamma_{ij}\langle\phi_i|\hat{T}+\hat{V}|\phi_j\rangle+\tfrac{1}{2}\sum_{i,j,k,l}\Gamma_{ijkl}\langle\phi_i\phi_j|r_{12}^{-1}|\phi_k\phi_l\rangle \tag{10}$$

corresponds to a wave function which is constrained to the HF density. If the density matrices Γ_{ij} and Γ_{ijkl} are kept frozen from the FCI calculation, Eq. (10) yields the upper bound to the functional $E_{\mathrm{FCI}}[\rho_{\mathrm{HF}}]$. Alternatively, one could recalculate the density matrices by diagonalizing an effective Hamiltonian which has terms related to derivatives of $\mathbf{S}$. Such an approach, which requires iterations of the FCI procedure, would result in exact (within the basis set used) values of $E_{\mathrm{FCI}}[\rho_{\mathrm{HF}}]$.

NUMERICAL METHODS

Calculations were carried out for the He atom, and the Li^+, Be^{2+}, B^{3+}, and C^{4+} cations. The HF densities were calculated using a quadratic grid

$$r_i=\tfrac{1}{2}i(i+1)s\ , \tag{11}$$

where the step s is determined by the number of grid points (equal to 50 000 in all calculations) and the cutoff. We found a proper choice of the cutoff to be crucial for obtaining an optimal numerical stability. Too small values of the cutoff yielded poor HF energies, while too large values caused difficulties with convergence in the DCFCI procedure. The cutoffs and the calculated HF energies are shown in Table I. The Laplace operator was discretized by a three-point approximation.

The basis sets used in the FCI and DCFCI calculations consisted of the s and p functions with their radial components obtained through Schmidt orthonormalization of the series

$$s_i(r)=\rho_{\mathrm{HF}}^{1/2}(r)r^{i-1},\quad i=1,2,\ldots \tag{12a}$$

$$p_i(r)=\rho_{\mathrm{HF}}^{1/2}(r)r^{i},\quad i=1,2,\ldots\ . \tag{12b}$$

The FCI Hamiltonians were diagonalized in the basis set of Slater determinants. All singly and doubly excited determinants were included. The necessary two-electron integrals were calculated by trapezoidal quadratures on a 50 000 point quadratic grid.

Density matrices frozen from the FCI wave functions were used in the DCFCI calculations. Therefore, our DCFCI results can be regarded as upper bounds to true DCFCI energies. However, we believe that, in the case of the helium series, relaxation of the density matrices would result in marginally improved energies (see the Discussion), while requiring an excessive amount of computational effort. Also, the density-constrained basis functions were computed using an approach slightly different from the one described in the previous section. The series, Eqs. (12a)–(12b), were Schmidt orthogonalized with the weight function

$$w(\mathbf{r})=\rho_{\mathrm{HF}}(\mathbf{r})\left[\sum_{i,j}\Gamma_{ij}\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\right]^{-1}\ . \tag{13}$$

The process was iterated until the resulting electron density differed from the HF density by less than 10^{-8} in average,

TABLE I. Values of the cutoffs used and the calculated HF energies in the helium series.

Z	Number of grid points	Cutoff (a.u.)	E_{HF} (a.u.)
2	50 000	10.0	−2.861 680
3	50 000	5.0	−7.236 415
4	50 000	3.0	−13.611 291
5	50 000	2.0	−21.986 048
6	50 000	2.0	−32.361 185

TABLE II. Convergence of the $l=0$ correlation energies of the helium atom.

N^{a}	e_{FCI}	e_{DCFCI}	$e_{\text{FCI}}-e_{\text{DCFCI}}$
2	−14 032.5	−13 923.8	−108.7
3	−15 703.5	−15 495.4	−208.1
4	−16 299.7	−16 055.7	−244.1
5	−16 802.6	−16 546.3	−256.3
6	−17 069.1	−16 778.4	−290.6
7	−17 192.4	−16 878.4	−314.0
8	−17 252.6	−16 928.2	−324.4
9	−17 285.9	−16 956.3	−329.5
10	−17 306.2	−16 973.5	−332.7
11	−17 319.2	−16 984.9	−334.4
12	−17 327.8	−16 992.5	−335.3
∞^{b}	−17 344.6±2.1	−17 008.2±0.6	−336.4±1.5
Literature	−17 348.7[c]		

[a] Number of the *s*-type basis functions. All energies are in μhartrees.

[b] See text for explanation of extrapolation and error estimates.

[c] Reference 13.

$$\int \left| \rho_{\text{HF}}(\mathbf{r}) - \sum_{i,j} \Gamma_{ij} \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) \right| d\mathbf{r} < 10^{-8} \; . \tag{14}$$

In a typical run, it took between 10 and 20 iterations to attain this level of convergence. We found such a procedure, while completely equivalent to Eqs. (7)–(9), to be numerically more stable.

The FCI and DCFCI energies at the $l=0$ (s) limit were obtained with the aid of Aitken extrapolation[12] using the results of calculations involving basis sets of 10, 11, and 12 s functions (10s-12s). The extrapolation errors were estimated as a difference between the extrapolated energies for the 10s-12s and 9s-11s calculations. The $l=1$ (p) limit results were obtained by first extrapolating the 12s9p-12s11p results to the 12$s\,\infty p$ limit and then adding corrections to account for the finite number of s functions. The corrections were estimated as the differences between the extrapolated energies for the $l=0$ (s) limit and the 12s results.

A typical 12s11p calculation (FCI and DCFCI) required about 700 s of CPU time on a CRAY Y-MP supercomputer. Most of the time was spent on numerical evaluation of the two-electron integrals. Since these integrals have to be recomputed in the DCFCI calculations, the FCI and DCFCI parts require approximately the same amount of computational effort.

RESULTS

The data on convergence of the FCI and DCFCI correlation energies of the helium atom to the $l=0$ (s) limit are presented in Table II. The extrapolated FCI correlation energy is within approximately 4 μhartree from the recently published value.[13] The difference $e_{\text{FCI}}-e_{\text{DCFCI}}$ converges substantially faster than the individual energies. This can be attributed to cancellation of the basis-set truncation errors. The extrapolated e_{DCFCI} correlation energy constitutes approximately 98% of the exact $l=0$ (s) limit correlation energy.

The $l=1$ (p) limit convergence, displayed in Table III, is as fast as the $l=0$ one. The extrapolated FCI correlation energy is within approximately 10 μhartree from the published data.[13] Quite surprisingly, inclusion of the p functions reduces the $e_{\text{FCI}}-e_{\text{DCFCI}}$ difference substantially. The extrapolated e_{DCFCI} accounts for more than 99.7% of the unconstrained $l=1$ (p) limit correlation energy.

The extrapolated $l=0$ and $l=1$ limit correlation energies are presented in Tables IV and V, respectively. The differences between the FCI and DCFCI energies decrease quadratically with the increasing atomic numbers Z. In fact, a plot of reciprocals of the square roots of the differences versus Z (Fig. 1) reveals that the approximate relations

TABLE III. Convergence of the $l=1$ correlation energies of the helium atom.

N^{a}	e_{FCI}	e_{DCFCI}	$e_{\text{FCI}}-e_{\text{DCFCI}}$
1	−28 931.9	−29 009.6	77.7
2	−35 723.9	−35 702.9	−20.9
3	−37 436.2	−37 392.2	−44.0
4	−38 019.6	−37 974.8	−44.8
5	−38 324.9	−38 279.6	−45.4
6	−38 506.2	−38 451.3	−54.9
7	−38 615.8	−38 549.2	−66.6
8	−38 682.9	−38 608.2	−74.7
9	−38 725.2	−38 645.9	−79.3
10	−38 752.6	−38 670.4	−82.2
11	−38 771.1	−38 687.2	−83.9
$12s\,\infty p^{\text{b}}$	−38 809.3±5.6	−38 723.8±7.9	−85.5±2.3
$\infty s\,\infty p$	−38 826.0±7.7	−38 739.4±8.6	−86.6±3.6
Literature	−38 836.2[c]		

[a] 12sNp basis sets. All energies are in μhartrees.

[b] See text for explanation of extrapolation and error estimates.

[c] Reference 13.

TABLE IV. The $l=0$ correlation energies in the helium series. All extrapolated energies are in μhartrees.

Z	e_{FCI}	e_{DCFCI}	$e_{\mathrm{FCI}}-e_{\mathrm{DCFCI}}$
2	$-17\,344.6\pm2.1$	$-17\,008.2\pm0.6$	366.4 ± 1.5
3	$-16\,073.0\pm1.5$	$-15\,968.9\pm2.4$	104.1 ± 1.0
4	$-15\,556.5\pm1.3$	$-15\,505.6\pm1.1$	-50.9 ± 0.2
5	$-15\,270.6\pm0.2$	$-15\,240.7\pm0.0$	-29.9 ± 0.2
6	$-15\,098.4\pm0.1$	$-15\,079.1\pm0.4$	-19.3 ± 0.3

$$E_{\mathrm{DCFCI}}-E_{\mathrm{FCI}}=e_{\mathrm{DCFCI}}-e_{\mathrm{FCI}}=541.9(Z-0.7301)^{-2}\ \mu\text{hartree}\ , \tag{15a}$$

for the $l=0$ limit, and

$$E_{\mathrm{DCFCI}}-E_{\mathrm{FCI}}=e_{\mathrm{DCFCI}}-e_{\mathrm{FCI}}=113.3(Z-0.8519)^{-2}\ \mu\text{hartree}\ , \tag{15b}$$

for the $l=1$ limit, are satisfied to a high degree of accuracy. The shifts in denominators of Eqs. (15a)–(15b) can be compared with the radius of convergence of the Z^{-1} series for the $l=\infty$ limit FCI energy, which is 0.91103.[14] Our conjecture is that the convergence radii of the Z^{-1} series for the $l=\infty$ limit of both E_{FCI} and $E_{\mathrm{FCI}}-E_{\mathrm{DCFCI}}$ are the same.

The presence of the Z^{-2} leading term in the difference between the FCI and DCFCI energies can be explained as follows: The Z^{-1} perturbation in the Z^{-2} scaled Hamiltonian

$$\hat{H}=-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2)-(r_1^{-1}+r_2^{-1})+Z^{-1}r_{12}^{-1} \tag{16}$$

that originates from the electron-electron repulsion results in a difference between the HF and FCI densities which is the order of Z^{-2}.[15] The two-electron integrals evaluated in the density-constrained basis set, Eqs. (7)–(9), differ from the original ones by the same order in Z. The resulting overall difference in the second-order term for the correlation energy (which is the leading term in this case) is of the order of Z^2 (from scaling of the Hamiltonian) multiplied by Z^{-2} (the second-order term) multiplied by Z^{-2} (the difference in integrals) equals Z^{-2}, as observed.

DISCUSSION: DYNAMICAL AND NONDYNAMICAL CORRELATION ENERGY

Although it is widely recognized that the electron-correlation energy is a sum of contributions from the dynamical and nondynamical correlation effects, a rigorous definition of these terms has not yet been proposed. Using the terminology of the independent particle theory, the dynamical correlation energy is vaguely described as the one originating from the interaction of the HF reference state with a large number of exited determinants. The coupling between the reference state and these determinants is assumed to be small. Systems in which only the dynamical electron correlation is important are easily described by a Hartree-Fock single-determinantal wave function with low-order perturbational corrections. The dynamical electron correlation originates from the Coulombic repulsion of the electrons and is sometimes termed the short-range correlation.[16]

On the other hand, the nondynamical correlation energy is a consequence of the existence of one, or a few, excited determinants that interact strongly with the HF reference state, usually due to pseudodegeneracy. Systems with significant amount of nondynamical, or long-range,[16] correlation energy usually cannot be correctly described within single-reference Hartree-Fock approximation. The nondynamical correlation energy plays important role in spin-polarized and metallic systems. Effort has been made to identify simple indices that would describe the relative importance of the two kinds of correlation energy.[17]

We propose that the correlation energy evaluated at the HF density, e_{DCFCI}, Eq. (3a), be regarded as the dynamical correlation energy, while the difference $e_{\mathrm{FCI}}-e_{\mathrm{DCFCI}}$ (which is always nonpositive) constitutes a definition of the nondynamical correlation energy. Both the correlation energies are supposed to be evaluated with respect to *the lowest energy solution* of the HF equa-

TABLE V. The $l=1$ correlation energies in the helium series. All extrapolated energies are in μhartrees.

Z	e_{FCI}	e_{DCFCI}	$e_{\mathrm{FCI}}-e_{\mathrm{DCFCI}}$
2	$-38\,826.0\pm7.7$	$-38\,739.4\pm8.6$	-86.6 ± 3.6
3	$-39\,468.3\pm5.5$	$-39\,446.2\pm7.9$	-22.2 ± 2.5
4	$-39\,806.9\pm4.5$	$-39\,795.2\pm4.4$	-11.7 ± 0.3
5	$-40\,007.4\pm1.3$	$-40\,000.9\pm1.7$	-6.5 ± 0.8
6	$-40\,141.6\pm1.1$	$-40\,137.4\pm1.2$	-4.2 ± 0.4

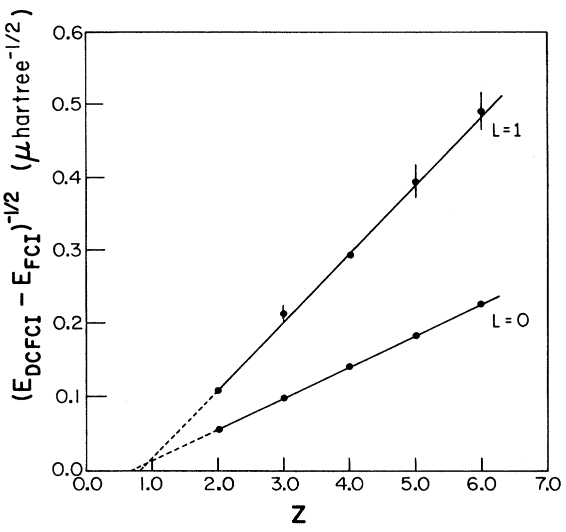

FIG. 1. Dependence of the nondynamical correlation energy on the nuclear charge in the helium series.

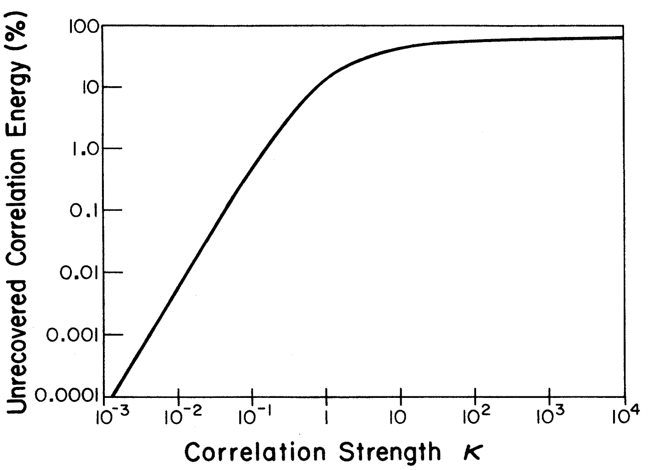

FIG. 2. Dependence of the unrecovered correlation energy on the correlation strength in a coupled harmonic-oscillator model, Eq. (17).

tions, even if it breaks the spatial and/or spin symmetry. This allows one to treat the dissociation limits of molecules in a consistent manner. The arguments supporting our definition are as follows:

(1) In systems in which there are no excited determinants strongly interacting with the HF reference state, the difference between the HF and FCI electron densities is expected to be small. This means that the difference $e_{\mathrm{FCI}} - e_{\mathrm{DCFCI}}$ is expected to be close to zero. This can be quantified using a model of N isolated Coulombic systems, each possessing n excited determinants separated by energy of Δ from the HF reference state and interacting through the Hamiltonian matrix element of V. From the second-order perturbation theory, the total correlation energy e_{FCI} is expected to be proportional to $-nNV^2\Delta^{-1}$. The difference between the HF and FCI densities is proportional to $NV^2\Delta^{-2}$. This results in the difference $e_{\mathrm{FCI}} - e_{\mathrm{DCFCI}}$ proportional to $-nN^2V^4\Delta^{-3}$, or $-e_{\mathrm{FCI}}^2/N\Delta$. One can therefore expect our definition of the nondynamical correlation energy to yield values inversely proportional to the energy gap Δ, which is exactly what one tries to describe by invoking the concept of pseudodegeneracy.

(2) A simple model of coupled harmonic oscillators is often invoked to illuminate the properties of theoretical techniques dealing with electron correlation.[18] The model is described by the Hamiltonian

$$\hat{H} = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2) + \tfrac{1}{2}(r_1^2 + r_2^2) + \tfrac{1}{2}\kappa r_{12}^2 \ , \tag{17}$$

where the coupling constant κ is the "correlation strength."

Using a trial function

$$\hat{\Psi} = A \exp[-a(r_1^2 + r_2^2) - b r_{12}^2] \ , \tag{18}$$

one arrives at (by setting $b=0$ and optimizing a) the "HF energy" of

$$F_{\mathrm{HF}} = 3(1+\kappa)^{1/2} \tag{19}$$

and (by optimizing both a and b) the "FCI energy" of

$$E_{\mathrm{FCI}} = \tfrac{3}{2}[1 + (1+2\kappa)^{1/2}] \ . \tag{20}$$

One can also constrain the parameter b in such a way that the resulting particle density is identical with the HF one, which yields the "DCFCI energy." In Fig. 2 we display the unrecovered correlation energy defined as $(e_{\mathrm{FCI}} - e_{\mathrm{DCFCI}})/e_{\mathrm{FCI}}$. For small values of κ, this fraction is proportional to κ^2, while for large κ's it reaches a constant limit. These two limiting behaviors reflect the "dynamical" and "nondynamical" correlation regimes.

The results of the calculations on the helium series clearly indicate that in this case the nondynamical effects are very small. The helium atoms and the corresponding cations are typical examples of the systems for which the HF wave function constitutes a good zeroth-order approximation. On the other hand, in the beryllium series one may expect the nondynamical correlation energy to be proportional to the nuclear charge Z, as is the total correlation energy.

We believe that our partitioning of the correlation energy into the dynamical and nondynamical parts will contribute to a better understanding of the advantages and limitations of the HF electron density functionals for the correlation energy. In particular, one is tempted to speculate that the current parametrizations of these functionals[19] recover only the nondynamical portion of the correlation energy.

ACKNOWLEDGMENTS

This research was partially supported by the U.S. Department of Energy under Contract No. DE-FC05-85ER25000 and by the Florida State University through time granted on its CRAY Y-MP digital computer. Support from the Camille and Henry Dreyfus Foundation is also acknowledged.

[1] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).

[2] See, for example, P. Saxe, H. F. Schaefer III, and N. C. Handy, Chem. Phys. Lett. **79**, 202 (1981).

[3] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).

[4] M. Levy, Proc. Natl. Acad. Sci. U.S.A. **76**, 6062 (1979); E. H. Lieb, Int. J. Quantum Chem. **24**, 243 (1983).

[5] P. W. Payne, J. Chem. Phys. **71**, 490 (1979).

[6] J. Cioslowski, J. Chem. Phys. **89**, 4871 (1988).

[7] P. O. Löwdin, Adv. Chem. Phys. **2**, 207 (1959), and references cited therein.

[8] R. A. Harris and L. R. Pratt, J. Chem. Phys. **83**, 4024 (1985); M. Levy, in *Density Matrices and Density Functionals,* edited by R. Erdahl and V. H. Smith, Jr. (Reidel, Dordrecht, 1987), pp. 479–498.

[9] J. Cioslowski, Phys. Rev. A **41**, 3458 (1990).

[10] J. Cioslowski, Phys. Rev. Lett. **60**, 2141 (1988).

[11] J. Cioslowski, Int. J. Quantum Chem. **S23**, 255 (1989).

[12] A. Ralston and P. Rabinowitz, *First Course in Numerical Analysis* (McGraw-Hill, New York, 1978), p. 358.

[13] S. Salomonson and P. Öster, Phys. Rev. A **40**, 5559 (1989)

[14] J. D. Baker, D. E. Freund, R. N. Hill and J. D. Morgan III, Phys. Rev. A **41**, 1247 (1990).

[15] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[16] R. McWeeny, in *The New World of Quantum Chemistry,* edited by B. Pullman and R. Parr (Reidel, Dordrecht, 1976).

[17] T. J. Lee, J. E. Rice, G. E. Scuseria, and H. F. Schaefer III, Theor. Chim. Acta **75**, 81 (1989), and references cited therein.

[18] P. Philips and E. R. Davidson, Int. J. Quantum. Chem. **23**, 185 (1983); L. Cohen and C. Lee, *ibid.* **S19**, 535 (1986); J. Cioslowski, *ibid.* **S21**, 563 (1987).

[19] E. Clementi, S. J. Chakravorty, and G. Corongiu, in *Modern Techniques in Computational Chemistry: MOTECC-89,* edited by E. Clementi (Escom, Leiden, 1989), and references cited therein.