PHYSICAL REVIEW A VOLUME 50, NUMBER 5 NOVEMBER 1994

Transfer of electron correlation from an electron gas to inhomogeneous systems via Jastrow factors

Heinz-Jürgen Flad* and Andreas Savin†
Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

(Received 15 February 1994)

In analogy to the local-density approximation of the density functional, a transfer of electron correlation from the homogeneous electron gas to inhomogeneous systems is realized through a density-dependent Jastrow factor. This approach enables a strictly variational treatment with respect to the inhomogeneous systems. We have adjusted the density-dependent Jastrow factor on the basis of electron-gas Jastrow factors, determined within a Fermi hypernetted-chain approximation. We applied it to the isoelectronic series He to Ne^{8+} where 83–90% of the correlation energy was recovered, taking into account a supplementary density-dependent one-particle Jastrow factor, which allowed an approximate conservation of the Hartree-Fock density. Within our simple application we are able to describe the electron correlation of different systems by means of a single Jastrow factor, which depends on the interelectronic distance and the electron densities at the positions of the electrons.

PACS number(s): 31.20.Di, 31.20.Tz

I. INTRODUCTION

Density functionals represent one of the most popular approaches for the treatment of electron correlation in quantum chemistry [1]. In its simplest form, the so-called local-density approximation (LDA) for closed-shell systems,

$$E_c = \int dV \rho(\mathbf{r}) \varepsilon(\rho(\mathbf{r})) \ , \tag{1}$$

to each volume element ΔV with given electron density $\rho(\mathbf{r})$, the corresponding correlation energy ε of the homogeneous electron gas, is adjoined. Although the deficiencies of this approach are well known (see, e.g., [1]) it provides a useful tool in molecular-structure calculations incorporating electron correlation. The LDA method raises the interesting question concerning the transferability of electron correlation from homogeneous to inhomogeneous systems. With the intention to investigate this problem, we pass over from the LDA approach because of its manifestly nonvariational nature.

The correlations within the homogeneous electron gas can be described with very high accuracy by Jastrow factors, as can be seen by a comparison of the Green-function Monte Carlo [2] and variational Monte Carlo (VMC) [3] correlation energies obtained with appropriate Jastrow factors. Our interest lies in the study of the possibility of transferring these Jastrow factors to inhomogeneous systems, an extreme case is that of the series He to Ne^{8+}, due to the fact that there are only two electrons present, to the small spatial extensions, and to the strong inhomogeneity of the densities. By using Jastrow factors we have strictly variational results and can expect that the errors in our ansatz will be reflected by an increase in energy. The Jastrow factors of the homogeneous electron gas,

$$F = \exp\left[\sum_{i<j} u_2(r_{ij},\rho)\right] \ , \tag{2}$$

depend explicitly on the electron-electron distances and implicit via adjusted parameters on the electron density. Obviously they cannot be transferred in a unique way because of the arbitrariness in assigning a density to an electron pair correlated in an inhomogeneous system. We treat this problem by choosing an averaged density.

In the solid-state case, electron-gas Jastrow factors were successfully applied [4,5]. Fahy, Wang, and Louie [4] could show for diamond and graphite that the optimal Jastrow factors are very close to electron-gas Jastrow factors corresponding to densities that are equal to the mean valence densities of the solids. Explicitly density-dependent Jastrow factors for inhomogeneous systems were introduced by Colle and Salvetti [6] within their nonvariational treatment of the energy expectation value, which shows some similarities with density-functional methods but without taking reference to the homogeneous electron gas. Their Jastrow factors were applied in a variational manner in VMC calculations [7]. Within the context of Monte Carlo calculations, density-dependent Jastrow factors were also discussed by Sun *et al.* [8].

II. TRANSFER FROM THE ELECTRON GAS

In order to transfer Jastrow factors from the homogeneous electron gas to inhomogeneous systems, it was at first necessary to determine optimal Jastrow factors for the homogeneous case which covered a wide range of densities. On the basis of these Jastrow factors we tried to determine a single density-dependent Jastrow factor, which describes for a fixed density the electron correlation in the homogeneous electron gas belonging to it.

---

*Present address: Max-Planck-Institut für Physik komplexer Systeme (Au*ß*enstelle Stuttgart), Heisenbergstrasse 1, 70569 Stuttgart, Germany.

†Present address: Laboratoire Dynamique des Interactions Moléculaires (CNRS, UPR 271), Université Pierre et Marie Curie, Tour 22, 4 place Jussieu, 75252 Paris Cedex 05, France.

The optimization procedure had to be carried out in a consistent manner because of the intended adjustment of density-dependent parameters. We have chosen the Fermi hypernetted-chain (FHNC) method within Krotscheck's FHNC//0 approximation (see, e.g., [9]), which was successfully applied to the homogeneous electron gas [10]. It was of special interest for us that it allowed for a fully numerical solution of the variational problem, because the parametrizations of the commonly employed electron-gas Jastrow factors [3] were designed for an optimal description of long-range correlations. On the contrary, we were interested in the short-range behavior. Therefore, we preferred the numerical solutions, which were not constricted by a parameter-dependent ansatz. Covering the whole range of densities from the vicinity of the nucleus up to the van der Waals radius, we determined Jastrow factors between $r_s = 0.1$ and $r_s = 5.0$,

$$r_s = \frac{1}{a_0}\left(\tfrac{4}{3}\pi\rho\right)^{-1/3} \tag{3}$$

(a_0 is the Bohr radius).

In the He series, the two electrons are confined to a small region of space. We thus put more emphasis in generating an accurate fit for the short and intermediate interelectronic distances than for the large ones. The value of u_2 for $r_{ij} = 0$ was thus of particular importance to us. It turns out that it has a marked dependence on the density. This value is unique for a given density of the homogeneous electron gas, as Jastrow factors are chosen to give the value 1 for large interelectronic distances. Therefore, it is useful to define a new function,

$$u_0(\rho) = u_2(0,\rho) \ , \tag{4}$$

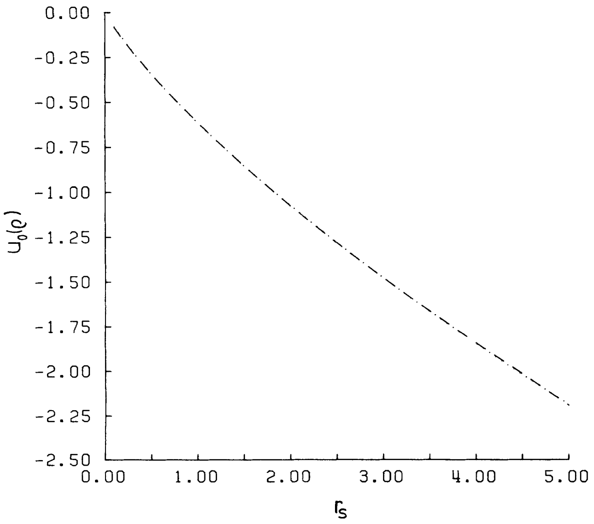

FIG. 1. Function $u_0(\rho)$, which characterizes the behavior of the FHNC//0 Jastrow factor at the electron-electron cusp. The plot shows the original function u_0 (— — —), together with its polynomial rational approximation (· · ·).

TABLE I. Parameters of the density-dependent functions $u_0(\rho)$ and $u_2(\rho, r_{ij})$.

b_1	−0.824 03
b_2	−0.459 96
b_3	1.046 95
b_4	0.036 26
c_1	−0.040
c_3	0.277

which depends only on the value of ρ. Figure 1 shows u_0 for r_s values between 0.1 and 5.0 at which we observed a nearly linear dependence with respect to r_s. As can be seen from Fig. 1, u_0 could be perfectly approximated within the considered range of densities by the polynomial rational function

$$u_0(\rho) = \frac{b_1 r_s + b_2 r_s^2}{1 + b_3 r_s + b_4 r_s^2} \ . \tag{5}$$

The attached parameters b_i (Table I) were determined by a simple least-squares fit. For the homogeneous electron gas, the behavior of u_2 for large electron-electron distances is well known [11]. We incorporated the asymptotic behavior as far as our ansatz was flexible enough to adopt it for appropriate chosen parameters. Based on these considerations, we have chosen the simple density-dependent ansatz

$$u_2 = \sum_{i<j} \frac{u_0 + c_1 r_{ij}}{1 + c_2 r_{ij} + (c_3 / r_s^{3/2}) r_{ij}^2} \tag{6}$$

for the function u_2. Furthermore, our Jastrow factor was forced to satisfy the electron-electron cusp condition for electrons with antiparallel spin [12]. It is therefore necessary that u_2 satisfies the boundary condition

$$\left.\frac{\partial u_2}{\partial r_{ij}}\right|_{r_{ij}=0} = \frac{1}{2} \ , \tag{7}$$

which if applied to ansatz (6) results in the relation

$$c_2 = \frac{1}{u_0}\left(c_1 - \tfrac{1}{2}\right) \tag{8}$$

between the coefficients c_1 and c_2. Together with the function u_0 it guarantees a correct behavior of u_2 up to linear terms in r_{ij}. Incorporating relation (8) in ansatz (6) yields the final form for u_2:

$$u_2 = \sum_{i<j} \frac{u_0 + c_1 r_{ij}}{1 + [(c_1 - \tfrac{1}{2})/u_0] r_{ij} + (c_3 / r_s^{3/2}) r_{ij}^2} \ . \tag{9}$$

At the very least, the parameters c_1 and c_3 were fixed in order to minimize the deviation between the FHNC Jastrow factors and our ansatz for short and medium electron-electron distances at various densities. It should be noticed that the ratio between c_1 and c_3 is not equal to that predicted by a direct application of the exact asymptotic behavior. This is due to the restricted flexibility of our ansatz for medium distances and our preference given to the short-range behavior. In view of the applications described in the next section, it will be without consequences because we have a correct fit for all occurring distances, cf. the final result depicted in Fig. 2, which shows good agreement between the FHNC Jastrow factors and our ansatz up to values of $r_{ij}=5r_s a_0$.

In order to transfer the density-dependent Jastrow factor (9) to inhomogeneous systems, we defined a mean density

$$\bar{\rho}_{ij}=\frac{\alpha}{2}[\rho(r_i)+\rho(r_j)]+(1-\alpha)\sqrt{\rho(r_i)\rho(r_j)} \tag{10}$$

with respect to the electron pairs. $\bar{\rho}_{ij}$ is composed of the arithmetic and geometric mean values from the densities at the positions of the two electrons. The parameter α can be treated variationally, as will be discussed in the next section. There are a lot of possible definitions for a mean density, but with regard to an intended subsequent application in quantum Monte Carlo calculations, we restricted ourselves to a definition that relied only on the densities at the positions of the electrons, because in this case the computational cost did not significantly increase [7].

Before one can apply the Jastrow factor (9) with the mean density (10) to inhomogeneous systems, it is important to notice that there arises an additional ambiguity besides the definition of the mean density. This is because of the trivial fact that in the case of the homogeneous electron gas the addition of a Jastrow factor to the Hartree-Fock (HF) wave function will not alter the given density. In contrast to this, we observed drastic density shifts in the case of a direct application of the Jastrow factor (9), in combination with a HF wave function, to inhomogeneous systems, as will be described in Sec. IV (see also [4]). Within density-functional theory, it was proved that it is wise to apply the correlation functional on the HF density [13]. Therefore, we based our method on the HF density, and in the following discussion all densities $\rho(r_i)$ in definition (10) will refer to HF. As a consequence, the Jastrow factor (9) was supplemented by a one-particle density-dependent Jastrow factor, which is characterized by the function $u_1(\rho)$. Obviously, this would be insignificant with respect to the homogeneous case, but it is suitable to restore the HF density for inhomogeneous systems [4]. In the spirit of density-functional theory, we looked for a system independent function $u_1(\rho)$, as will be described in Sec. IV. Our final ansatz for the correlated wave functions of inhomogeneous systems,

$$\Psi=\prod_i e^{u_1(\rho_i)}\prod_{i<j} e^{u_2(r_{ij},\bar{\rho}_{ij})}\Phi_{\mathrm{HF}}\ , \tag{11}$$

could be viewed as a Jastrow factor analog to the density functional (1).

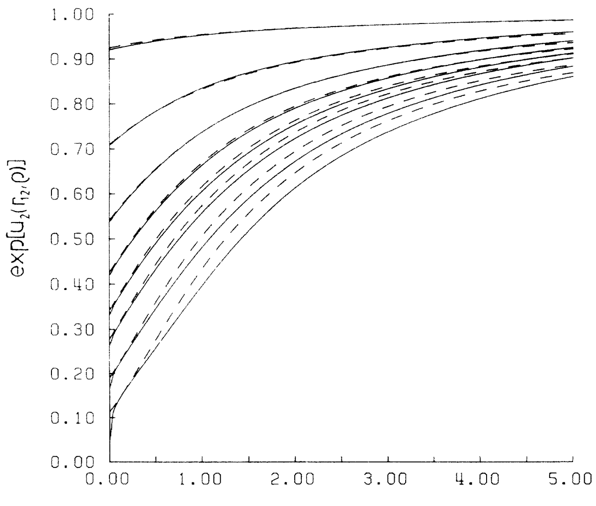

FIG. 2. Comparison of the FHNC//0 Jastrow factors (——) and our ansatz for a density-dependent Jastrow factor (— — —) for fixed electron densities. The corresponding densities are given by $r_s=0.1,0.5,1.0,1.5,2.0,2.5,3.5,5.0$ (r in atomic units).

III. APPLICATION TO THE ISOELECTRONIC SERIES He TO Ne^{8+}

In the following, we will discuss the application of our approach to a simple model that consists of the isoelectronic row of two electron systems He to Ne^{8+}. Before tackling the determination of the function u_1, we had to specify the parameter α in definition (10). Since α is directly related to the electron correlation, we have optimized it together with the orbitals in the wave functions,

$$\Psi_1=e^{u_2(r_{12},\bar{\rho}_{12})}\varphi_{\mathrm{opt}}(r_1)\varphi_{\mathrm{opt}}(r_2)\ , \tag{12}$$

in order to minimize the variance of the local energy. This was done for each system separately. The optimization was realized by making use of quantum Monte Carlo techniques where this criterion is commonly employed [14]. HF orbitals for the two electron systems were taken from Clementi and Roetti [15]. These orbital coefficients and $\alpha=0.5$ provided the starting point for the variance optimization. We added to each basis set an additional diffuse basis function that was determined in an even tempered manner from the ratio of the two smallest exponents in order to oppose the function u_2, which accumulates the density in the region near the nucleus, as can be seen in Fig. 3. As a result, for α we obtained 0.29, 0.23, 0.23 in the case of He, Li$^+$, Be^{2+} and 0.0 for the ions B^{3+} to Ne^{8+}. Therefore, we decided to use $\alpha=0.0$ in all cases because it is essential to choose a common value for α if the idea of system independent functions u_1, u_2 should be maintained.

IV. DETERMINATION OF u_1

Within this model, we have determined the function u_1 by the following course of arguments. At first, we demanded for u_1 to be independent of the atomic number Z. Secondly, u_1 should be chosen in such a way as to preserve the HF density, which is for these systems very close to the exact density. These are necessary conditions with respect to the intended analogy to the LDA (1) of density-functional theory.

The last condition could be applied in an easy way to each system separately by optimizing the orbitals φ of the

TABLE II. Variational energies and standard deviations of the local energy (in atomic units) for the wave functions Ψ_1 and Ψ_3 calculated by VMC. The statistical errors with respect to the total energy are given in parentheses.

Z^a	Ψ_1	$E_c{}^b$	σ^c	Ψ_3	$E_c{}^b$	σ^c
2	−2.9016(5)	95	0.15	−2.8992(4)	89	0.29
3	−7.2772(6)	94	0.24	−7.2757(6)	90	0.43
4	−13.6528(3)	94	0.33	−13.6508(11)	89	0.63
5	−22.0280(6)	93	0.46	−22.0263(9)	90	0.78
6	−32.4019(10)	90	0.62	−32.4007(11)	88	0.95
7	−44.7765(10)	89	0.71	−44.7755(11)	87	1.11
8	−59.1516(13)	89	0.88	−59.1498(11)	85	1.31
9	−75.5260(11)	88	0.97	−75.5251(11)	86	1.52
10	−93.9003(11)	86	1.17	−93.8991(11)	83	1.70

[a] Atomic number.

[b] Correlation energy (%).

[c] Standard deviation of the local energy.

wave functions Ψ_1 in order to obtain the HF density from it. As we have nodeless orbitals, we can equate the wave functions Ψ_1 and

$$\Psi_2=e^{u_{1z}(\rho_1)}e^{u_{1z}(\rho_2)}e^{u_2(r_{12},\bar{\rho}_{12})}\varphi_{\mathrm{HF}}(r_1)\varphi_{\mathrm{HF}}(r_2)\ , \tag{13}$$

where the latter is equivalent to wave function (11), in order to obtain the functions u_{1z} from the equation

$$u_{1z}(\rho)=\ln[\varphi_{\mathrm{opt}}(r(\rho))/\varphi_{\mathrm{HF}}(r(\rho))]\ . \tag{14}$$

This could be done because for the systems under consideration there is a unique relation between the radial distance r and the density ρ. The orbital coefficients in Eq. (12) were optimized by a simplex algorithm [16], whereby the required densities with respect to the wave function (12) were calculated by numerical integrations. We used the formula of Coulson and Neilson [17], where the volume element of an integrand with spherical symmetry was given with respect to the variables r_1,r_2,r_{12}. The integration could be carried out by successive numerical integrations in one dimension. After we had finished the optimization with respect to the density, we determined the energies belonging to the wave functions (12) by VMC calculations, which yielded between 86 and 95 % of the correlation energy (Table II). For our VMC calculations, we have used a generalized Metropolis algorithm, which is equivalent to a diffusion Monte Carlo algorithm without branching [18].

At this point, we have to ask for our first demand, which referred to the conformity of the functions u_{1z}. Figure 3 shows the functions u_{1z} calculated from Eq. (14) for the various systems. The curves in Fig. 3 are almost parallel, which means that we got at least a first qualitative confirmation of our approach, because it is, of course, possible to shift the functions u_{1z} along the ordinate without altering the results. We carried out these parallel shifts for the functions u_{1z} of the systems He to F^{7+} in order to obtain a minimal deviation to the function u_{1z} of Ne^{8+}. An excellent agreement could be observed for B^{3+} to Ne^{8+} but also slight deviations for Li$^+$ and Be^{2+} as well as a larger deviation in the high-density region for He. This behavior was not unexpected if one takes into account the special position of He, Li$^+$, Be^{2+} on optimizing the α parameters in definition (10). Therefore, we choose points only from the curves of B^{3+} to Ne^{8+} and adjusted a polynomial rational function

$$u_1(\rho)=\frac{a_0+a_1r_s+a_2r_s^2}{1+a_3r_s+a_4r_s^2}\ , \tag{15}$$

as can be seen in Fig. 4. The parameters a_i are listed in Table III. We were now able to define wave functions for these systems,

$$\Psi_3=e^{u_1(\rho_1)}e^{u_1(\rho_2)}e^{u_2(r_{12},\bar{\rho}_{12})}\varphi_{\mathrm{HF}}(r_1)\varphi_{\mathrm{HF}}(r_2)\ , \tag{16}$$

where the electron correlation depends only on the electron density and the electron-electron distance. All parameters in the functions u_1 and u_2 are independent from the atomic number of the system under consideration. It becomes apparent from Table II that the wave functions

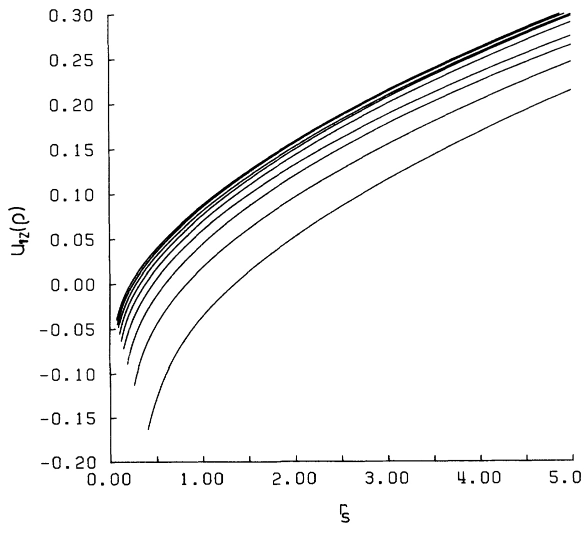

FIG. 3. Functions $u_{1z}(\rho)$ for He to Ne^{8+}, resulting from optimizations with respect to their densities.

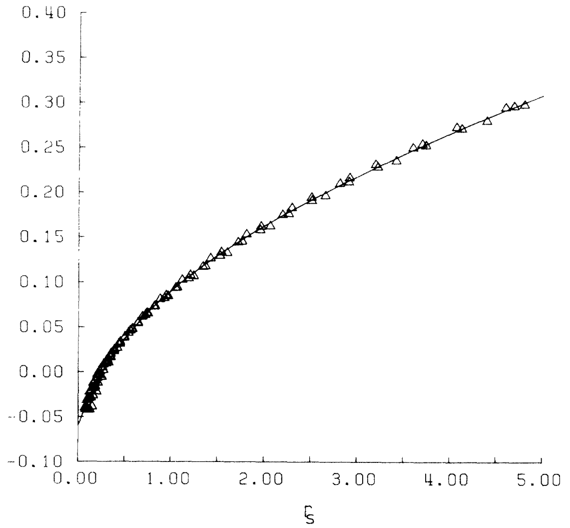

FIG. 4. Function $u_1(\rho)$ together with the points Δ, obtained from the functions u_{1z} of Fig. 3 after shifts along the ordinate, which were used for the adjustment of the parameters.

TABLE III. Parameters of the density-dependent function $u_1(\rho)$, adjusted with respect to the functions $u_{1z}(\rho)$ for B^{3+} to Ne^{8+}.

a_0	−0.061 04
a_1	0.209 93
a_2	0.092 00
a_3	1.604 88
a_4	0.065 39

Ψ_3 recover nearly the whole correlation energy that was obtained with Ψ_1. To be more precise, we lost between 4% and 6% of the correlation energy for He, Li^+, Be^{2+}, and 2% to 3% for the other systems. Another very sensitive criterion is the standard deviation of the local energy [14], which is also listed in Table II. In going from Ψ_1 to Ψ_3, we observed a considerable worsening of this quantity. This is due to the behavior of the wave function in the vicinity of the nucleus. In the case of Ψ_1, the wave functions could satisfy the electron-nucleus cusp conditions through an appropriate optimization of their orbitals. Instead of this, the behavior of Ψ_3 near the nucleus of a given system is impaired, through the function u_1, by the other systems with different electron densities at their nuclei. As can be seen in Fig. 4, the largest fluctuations of the points occurred in the high-density region below $r_s=0.5$.

V. CONCLUSIONS AND OUTLOOK

We described a procedure for the transfer of electron correlation from the homogeneous electron gas to inhomogeneous systems in the case of the simple two-electron systems He to Ne^{8+}. In view of its variational character, this is an appealing alternative in comparison to similar approaches in density-functional theory. It would now be tempting to apply the whole machinery to more complicated systems. Unfortunately, it is not possible to use the wave function (11) with the above determined functions u_1 and u_2 directly. This is due to the fact that the described mean density (10) becomes meaningless for large electron-electron distances. Already in the case of the Li atom, we got an inadequate description of core-valence correlation. In order to extend the above method to larger systems, one has to restrict the sphere of action with respect to the Jastrow factor. This possibility is currently under investigation.

ACKNOWLEDGMENT

We would like to thank Professor E. Krotscheck for providing us with his FHNC//0 program and for informative discussions about the FHNC method.

---

[1] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, England, 1989); T. Ziegler, Chem. Rev. **91**, 651 (1991).

[2] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[3] D. M. Ceperley, Phys. Rev. B **18**, 3126 (1978).

[4] S. Fahy, X. W. Wang, and S. G. Louie, Phys. Rev. Lett. **61**, 1631 (1988); Phys. Rev. B **42**, 3503 (1990).

[5] S. Tanaka, J. Phys. Soc. Jpn. **62**, 2112 (1993).

[6] R. Colle and O. Salvetti, Theor. Chim. Acta **37**, 329 (1975); **53**, 55 (1979).

[7] J. W. Moskowitz, K. E. Schmidt, M. A. Lee, and M. H. Kalos, J. Chem. Phys. **76**, 1064 (1982); R. J. Harrison and N. C. Handy, Chem. Phys. Lett. **113**, 257 (1985).

[8] Z. Sun, P. J. Reynolds, R. K. Owen, and W. A. Lester, Jr., Theor. Chim. Acta **75**, 353 (1989).

[9] J. W. Clark, in *Progress in Particle and Nuclear Physics,* edited by D. H. Wilkinson (Pergamon, Oxford, 1979), Vol. 2, p. 89.

[10] E. Krotscheck, Ann. Phys. (NY) **155**, 1 (1984); E. Krotscheck, W. Kohn, and G. X. Qian, Phys. Rev. B **32**, 5693 (1985).

[11] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

[12] R. T. Pack and W. Byers Brown, J. Chem. Phys. **45**, 556 (1966).

[13] H. Stoll and A. Savin, in *Density Functional Methods in Physics,* edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985), p. 177.

[14] C. J. Umrigar, K. G. Wilson, and J. W. Wilkins, Phys. Rev. Lett. **60**, 1719 (1988); in *Computer Simulation Studies in Condensed Matter Physics: Recent Developments,* edited by D. P. Landau, K. K. Mon, and H. B. Schüttler (Springer-Verlag, Berlin, 1988).

[15] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

[16] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes: The Art of Scientific Computing* (Cambridge University Press, Cambridge, England, 1986).

[17] C.A. Coulson and A. H. Neilson, Proc. Phys. Soc. **78**, 831 (1961).

[18] B. H. Wells, in *Electron Correlation in Atoms and Molecules,* edited by S. Wilson (Plenum, New York, 1987), p. 311.