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# Improvement on the correlated-Hartree-Fock method and application to atoms

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Based on the recent paper of Yasuhara and Takada [Phys. Rev. B **43**, 7200 (1991)] on a screened-exchange potential for band calculations, an improvement is made on the correlated Hartree-Fock method for inhomogeneous many-electron systems so as to yield excellent results for both the total energies and the ionization potentials of atoms in the Periodic Table from He to Ca.

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## I. INTRODUCTION

Conventionally, the ground-state energy of a many-electron system, $E_0$, is broken down into the Hartree, exchange, and correlation parts:

$$E_0=E_H+E_x+E_c \ . \tag{1.1}$$

In practical calculations of $E_0$ in real solids, molecules, and even atoms, we must introduce some approximate scheme to evaluate the exchange and correlation parts, $E_x+E_c$. The most notable is the local-density approximation (LDA) based on the density-functional theory (DFT) [1–3]. However, LDA provides results with moderate accuracy (typically 1–10 %) [4,5] and thus an improvement on it is needed if better accuracy is required. For this purpose, both the self-interaction correction [6,7] and the gradient correction [8–10] are developed within the framework of DFT.

If we consider the correction to LDA in perturbation-theoretic approaches, we quite naturally hit upon an idea that at least $E_x$ should be treated more seriously by the consideration of its *nonlocal* character, because $|E_x|$, which has a very nonlocal feature [11], is definitely much larger than $|E_c|$ at metallic densities. As an extreme in this direction, we can think of the following scheme: We first solve the self-consistent Hartree-Fock (HF) equations to obtain $E_H+E_x$ and then evaluate $E_c$ in the local approximation, a modification of LDA to $E_x+E_c$, with the electronic density obtained in the first step. At first sight, this seems to be a physically correct procedure, because the radius of the correlation hole is about half of the exchange hole in the homogeneous electron gas and thus nonlocality is less serious in $E_c$ than in $E_x$. However, according to the calculation of $E_0$ for atoms in this scheme [12,13], a systematic error is found: The calculated values of $E_0$ are always lower than the experimental ones. The situation does not change at all even if we perform the full self-consistent procedure in which the effect of $E_c$ is included in the solution of the HF equations, as we shall show in this paper by the HF+C scheme. This implies that the local-potential approximation to $E_c$ should be corrected in some way.

A different scheme to include nonlocality can be considered by an alternative partition of the exchange and correlation energies in $E_0$: As indicated in the so-called GW approximation [14–17], $E_0$ may be rewritten as

$$E_0=E_H+E_{\mathrm{SE}}+E_{Ch} \ , \tag{1.2}$$

where the screened-exchange part $E_{\mathrm{SE}}$ is defined by the exchange energy with some static screened potential $V_{\mathrm{sc}}$ rather than the bare Coulomb potential $V^0$ and $E_{Ch}$ represents the Coulomb-hole energy. Based on this partition, proposals [18,19] have been made to perform the HF procedure with $V_{\mathrm{sc}}$ rather than $V^0$ for the exchange part. In this approach, $E_{Ch}$ is usually treated in the local approximation, but the problem lies in the fact that $|E_{\mathrm{SE}}|$ does not dominate over $|E_{Ch}|$ in the partition (1.2). This means that errors in the evaluation of $E_{Ch}$ by the local approximation may become even more serious in this case. A tentative calculation of $E_0$ for atoms in the Yasuhara-Takada scheme [19], which is one of the methods in this approach and will be denoted by CHF (correlated Hartree-Fock) hereafter, shows that the results of $E_0$ are always larger than the experimental ones. Thus we come to conclude that at least in the calculation of $E_0$ for atoms, nonlocality in $E_{Ch}$ should not be neglected in CHF.

In view of those situations, we propose a combination of HF+C and CHF for an *ab initio* calculation of the properties of atoms and molecules in this paper. To be

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more specific, let us start with HF+C. Then the problem is to include nonlocality in $E_c$. A practical form for the nonlocality may be obtained if we compare Eq. (1.1) with Eq. (1.2). In CHF, $E_{\mathrm{SE}}$ is treated as nonlocal, which means that the difference $E_{\mathrm{SE}}-E_x$ represents the nonlocal part in $E_c$ in the partition (1.1). Of course, the full value of $E_{\mathrm{SE}}-E_x$ is not necessarily the best choice. So we introduce a multiplicative factor $\eta$ in front of it so as to give yet another partition for $E_0$ as

$$E_0=E_H+E_x+\eta(E_{\mathrm{SE}}-E_x)+E_{\mathrm{lc}} \; . \tag{1.3}$$

Here both $E_x$ and $E_{\mathrm{SE}}$ will be treated exactly as in the HF method and $E_{\mathrm{lc}}$ is the correlation contribution in the local approximation. The local potential to define $E_{\mathrm{lc}}$ depends on $\eta$ and is determined in such a way that in the homogeneous electron gas, $E_0$ in Eq. (1.3) reproduces the exact total energy known by other many-body methods such as the Green's-function Monte Carlo. Note that HF+C and CHF correspond, respectively, to the cases of $\eta=0$ and 1 in Eq. (1.3).

In the partition (1.3), the main issue is the value for $\eta$ in order to obtain a systematic agreement between theory and experiment, together with a suitable form for $V_{\mathrm{sc}}$ to define $E_{\mathrm{SE}}$. This constitutes the main purpose of this paper. After self-consistent calculations of $E_0$ as well as the ionization potentials for the atoms in the Periodic Table from He to Ca in the present approach with change of $\eta$, we find that an optimum value for $\eta$ is $\frac{2}{3}$.

This paper is organized as follows: In Sec. II we give a brief description of CHF in the Yasuhara-Takada version to define $V_{\mathrm{sc}}$ to be used in this paper. In the final part of this section, we introduce $\eta$ to combine CHF with HF+C. In Sec. III the CHF equations are reduced to the form convenient for the calculation of atomic properties. An approximate, but very accurate expression for $E_0$ in CHF is presented here. Calculated results for the total energies, the energy levels, and the ionization potentials are shown in Sec. IV. Summary of the results obtained in this paper and future problems are given in Sec. V. Rydberg units ($\hbar=e^2/2=1, m_e=\frac{1}{2}$) will be employed in the derivation of equations in this paper. In the tables and figures, however, the calculated energies are presented in atomic units, because most of the results published so far are given in those units.

## II. GENERAL FORMULATION OF CHF AND COMBINATION WITH HF+C

The CHF equation with nonlocal screened-exchange and local correlation potentials proposed by Yasuhara and Takada [19] is given as

$$\left[-\nabla^2-\frac{2Z}{r}+2\sum_{j\sigma'}n_{j\sigma'}\int d\mathbf{r}'\frac{f^*_{j\sigma'}(\mathbf{r}')f_{j\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\tilde{\mu}_{\mathrm{xc}}[r_s(n(\mathbf{r}))]\right]f_{i\sigma}(\mathbf{r})$$
$$-2\sum_{j\sigma'}\delta_{\sigma\sigma'}n_{j\sigma'}\int d\mathbf{r}'\frac{f^*_{j\sigma'}(\mathbf{r}')f_{i\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|\tilde{\varepsilon}(\mathbf{r}-\mathbf{r}')}f_{j\sigma'}(\mathbf{r})=\varepsilon_{i\sigma}f_{i\sigma}(\mathbf{r}) \; , \tag{2.1}$$

where $Z$ is the atomic number and $n_{i\sigma}$ represents the electron occupation number of state $i$ with spin $\sigma$ described by the wave function $f_{i\sigma}(\mathbf{r}')$. The dielectric function $\tilde{\varepsilon}(\mathbf{r}-\mathbf{r}')$ is introduced to define $V_{\mathrm{sc}}$ as

$$\begin{aligned}V_{\mathrm{sc}}(\mathbf{r}-\mathbf{r}')&\equiv\frac{1}{|\mathbf{r}-\mathbf{r}'|}\frac{1}{\tilde{\varepsilon}(\mathbf{r}-\mathbf{r}')}\\&=\int\frac{d\mathbf{q}}{(2\pi)^3}e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\frac{v(q)}{\tilde{\varepsilon}(q)} \; ,\end{aligned} \tag{2.2}$$

with

$$\tilde{\varepsilon}(q)=1+\Gamma(q)v(q)\Pi^0(q) \; , \tag{2.3}$$

where $v(q)$ is the Fourier coefficient of the bare Coulomb potential $V^0$, $\Pi^0(q)$ is the static polarization function in the random-phase approximation, and $\Gamma(q)$ is given through the so-called local-field factor (LFF) $G(q)$ as

$$\Gamma(q)=\frac{[1-G(q)]^2}{1+G(q)[1-G(q)]v(q)\Pi^0(q)} \; . \tag{2.4}$$

We need not specify the form for $G(q)$ to make a further development of the general formulation of CHF, but for the homogeneous electron gas with the electronic density characterized by the parameter $r_s$ in the usual definition, a tentative form for $G(q)$ is suggested in Ref. [19] as

$$G(z)=\frac{4Az^2}{1+4Bz^2} \; . \tag{2.5}$$

Here $z\equiv\alpha r_s q/2$ with $\alpha=(4/9\pi)^{1/3}=0.5211$ and the coefficients $A$ and $B$ are, respectively, given in Eqs. (A1) and (A2) in the Appendix. With the use of the variable $z$, we can rewrite the product of $v(q)$ and $\Pi^0(q)$ in Eqs. (2.3) and (2.4) as

$$v(q)\Pi^0(q)=\frac{\lambda^2}{8z^2}P(z) \; , \tag{2.6}$$

with

$$\lambda\equiv\left[\frac{4\alpha r_s}{\pi}\right]^{1/2} \tag{2.7}$$

and

$$P(z)=1+\frac{1-z^2}{4z}\ln\frac{(1+z)^2}{(1-z)^2} \; . \tag{2.8}$$

Then we can calculate $\tilde{\varepsilon}(\mathbf{r}-\mathbf{r}')$ from Eqs. (2.3), (2.4), (2.6), and (2.8).

In Eq. (2.1), the local potential $\tilde{\mu}_{\mathrm{xc}}$ is defined as

$$\tilde{\mu}_{\mathrm{xc}}=\mu_c+\tilde{\mu}_x \; , \tag{2.9}$$

with

$$\tilde{\mu}_x = -\frac{16}{\pi^2\lambda^2}\int_0^1 dz\,(1-z)\tilde{S}(z) \tag{2.10}$$

and

$$\tilde{S}(z) = 1 - \frac{1}{\tilde{\varepsilon}(z)} . \tag{2.11}$$

The correlation contribution to the chemical potential in Eq. (2.9), $\mu_c$, is the same as that given by Vosko, Wilk, and Nusair [20]. If $G(q)$ is chosen in the form (2.5), the local exchange potential in Eq. (2.10), $\tilde{\mu}_x$ is calculated analytically. The result is given in Eq. (A3) in the Appendix. With those $\tilde{\varepsilon}(\mathbf{r}-\mathbf{r}')$ and $\tilde{\mu}_{xc}$ thus determined, we can obtain the one-electron energy level and the wave function for each quantum state in the CHF scheme by the self-consistent solution of Eq. (2.1).

In order to combine CHF with HF+C [12,13], we only need to introduce a parameter $\eta$ to control the magnitude of $E_{SE}-E_x$. For this purpose, we first change $V_{sc}$ in Eq. (2.2) into

$$V_{sc} \rightarrow V^0 + \eta(V_{sc} - V^0) . \tag{2.12}$$

Then we also change the factor $\tilde{S}(z)$ in Eq. (2.10) into

$$\tilde{S}(z) \rightarrow \eta\tilde{S}(z) , \tag{2.13}$$

in order to obtain a corresponding change in $\tilde{\mu}_{xc}$ in Eq. (2.9). Note that $\eta=1$ corresponds to CHF, while $\eta=0$ corresponds to HF+C.

## III. SPECIFICATION TO ATOMS

### A. CHF equation

The nonlinear differential equation (2.1) is transformed into an expression convenient for the calculation of atomic wave functions and eigenenergies. For the practical solution of Eq. (2.1), we make two assumptions for the wave function $f_{i\sigma}(\mathbf{r})$ at the outset: One is the central-field approximation as is usually presumed in the atomic calculation in HF. The other is that the radial part of $f_{i\sigma}(\mathbf{r})$ does not depend on either magnetic or spin quantum number. This means that we shall take a treatment similar to the so-called *restricted* Hartree-Fock equation.

Under those assumptions, the wave function is divided into the factors as

$$f_{i\sigma}(\mathbf{r}) \equiv \frac{1}{r}P_{nl}(r)Y_l^m(\hat{\mathbf{r}})\chi(\sigma) , \tag{3.1}$$

with the radial function $P_{nl}(r)$, the spherical harmonics $Y_l^m(\hat{\mathbf{r}})$, and the spin function $\chi(\sigma)$, where $n$, $l$, and $\sigma$ denote, respectively, principal, angular, and spin quantum numbers. Substituting Eq. (3.1) into Eq. (2.1), we obtain the following nonlinear inhomogeneous equation:

$$\left[-\frac{d^2}{dr^2} - \frac{2Z}{r} + \frac{l(l+1)}{r^2} + V_c(r) + \tilde{\mu}_{xc}[\rho(r)] - \varepsilon_{nl}\right] \times P_{nl}(r) = \tilde{F}_{nl}(r) , \tag{3.2}$$

in which $V_c(r)$ and $\tilde{F}_{nl}(r)$ are the Hartree potential and the screened Fock term, respectively. The normalization condition for the radial function $P_{nl}(r)$ is given as

$$\int_0^\infty P_{nl}(r)^2 dr = 1 , \tag{3.3}$$

and the total electron density is obtained as

$$\rho(r) = \sum_{nl} N_{nl}P_{nl}(r)^2 , \tag{3.4}$$

where $N_{nl}$ is the occupation number of the state specified by $(n,l)$. With this charge density, the Hartree potential is calculated easily as

$$V_c(r) = \frac{2}{r}\int_0^r \rho(r')dr' + \int_r^\infty \frac{2}{r'}\rho(r')dr' . \tag{3.5}$$

In the treatment of the nonlocal term in Eq. (2.1), care must be taken in calculating the $LS$-term energy which is important in complex atoms. The concept of Slater's "average energy of the configuration" [21] is employed to treat it to obtain the nonlocal term $\tilde{F}_{nl}(r)$ in Eq. (3.2) as

$$\tilde{F}_{nl}(r) = 2P_{nl}(r)\left[J^0_{nl,nl}(r) + \sum_{L=2,4,\ldots}\left[\frac{N_{nl}-1}{4l+1}c^L(l0;l0) - \frac{2}{N_{nl}}D^L(l)\right]J^L_{nl,nl}(r)\right] + \sum_{n'l'\neq nl} N_{n'l'}P_{n'l'}(r)\left[\frac{1}{\sqrt{(2l+1)(2l'+1)}}\sum_L c^L(l0;l0)J^L_{nl,n'l'}(r)\right] , \tag{3.6}$$

with

$$J^L_{nl,n'l'}(r) = \int_0^\infty dr' P_{nl}(r')P_{n'l'}(r')U^L(r,r') , \tag{3.7}$$

$$U^L(r,r') = \frac{r_<^L}{r_>^{L+1}} - Q^L(r,r') , \tag{3.8}$$

and

$$Q^L(r,r') = \frac{2}{\pi}\int_0^\infty dq\,\tilde{S}(q;\bar{r}_s)j_L(qr)j_L(qr') , \tag{3.9}$$

where $c^L(lm;l'm')$ is the Inglis-Shortley coefficient [22] and $D^L(l)$ is the coefficient accounting for the deviation from the average energy of the configuration [23]. In Eq. (3.8), $r_<$ and $r_>$ represent, respectively, smaller and greater between $r$ and $r'$, while in Eq. (3.9), $j_L(x)$ denotes the spherical Bessel function of order $L$ and $\tilde{S}(q;\bar{r}_s)$ is the function $\tilde{S}(q)$ defined in Eq. (2.11) evaluated at $r_s=\bar{r}_s$. Here $\bar{r}_s$ is meant as some average of the $r_s$ parameter. Although the best choice for the average is not known at present, we employ the arithmetic mean between $r_s(r)$

and $r_s(r')$ for $\bar{r}_s$ in this paper, where the $r_s$ parameter at the position $r$, $r_s(r)$, is determined from the total electron density $\rho(r)$ in Eq. (3.4).

### B. Numerical procedure

Calculation procedures in HF or its modification may be classified into two categories: analytical or numerical. The representative in the former is the well-known Roothaan method [24] in which the problem is reduced to a generalized eigenvalue problem by the expansion in terms of the optimized-Gaussian or Slater-orbital basis. In the latter, a direct numerical integral of the HF nonlinear equation is performed [25]. In this paper, we proceed along the latter procedure.

In order to obtain the radial wave function numerically, we introduce grid units on which the wave function is given. The grid points are defined by the logarithmic variable and the Numerov algorithm is employed in the solution of Eq. (3.2). A self-consistent result is obtained by an iteration method in which we start with the wave function self-consistently determined in LDA. The total charge density is made self-consistent with the Liberman-Waber-Cromer program [25] based on a relativistic Hartree-Fock-Slater equation. The inhomogeneous term in Eq. (3.2), $\tilde{F}_{nl}(r)$, is evaluated with the radial wave function obtained in the previous iteration step and thus it is a known quantity for the present iteration. Then the combined shooting-direct method for an inhomogeneous equation [26] is employed to give an inhomogeneous solution to Eq. (3.2) which is made continuous at the classical turning point by the matching of inward and outward wave functions. This matching is made possible by the correction to the energy. For the correction, the usual method in a Hartree-Fock-Slater atomic calculation [27] is extended in the inclusion of the nonlinear Fock term. Since the inhomogeneous solution does not always satisfy Eq. (3.3), a homogeneous solution is added to it to maintain the normalization condition (3.3).

### C. Expression for the total energy

The total energy $E_0$ is an important physical quantity by which a theory can be tested. In Ref. [19], no expression for $E_0$ was given, primarily because the formally exact expression is quite difficult to obtain in CHF. In this subsection, we give an approximate but accurate enough expression for $E_0$. The basic strategy is to divide $E_0$ into local and nonlocal parts. Then the former is treated in an analogous way to LDA, while the latter to HF. Let us give our expression first:

$$E_0=E_0^{(1)}+E_0^{(2)} \ , \tag{3.10}$$

with

$$\begin{aligned}E_0^{(1)}=&\sum_{nl}N_{nl}\varepsilon_{nl}-\tfrac{1}{2}\int_0^\infty dr\,\rho(r)V_c(r)\\&+\int_0^\infty dr\,\rho(r)\{\tilde{\varepsilon}_{xc}[\rho(r)]-\tilde{\mu}_{xc}[\rho(r)]\}\\&+\tfrac{1}{2}\sum_{nl}N_{nl}\int_0^\infty dr\,P_{nl}(r)\tilde{F}_{nl}(r) \ ,\end{aligned} \tag{3.11}$$

and

$$E_0^{(2)}=\frac{2}{\pi}\int_0^\infty dq\sum_{nl}N_{nl}\left[I_{nl}^0(q)+\sum_{L=2,4,\ldots}\left[\frac{N_{nl}-1}{4l+1}c^L(l0;l0)-\frac{2}{N_{nl}}S^L(l)\right]I_{nl}^L(q)\right] \ , \tag{3.12}$$

where $\rho_{nl}(r)$ is the partial electron density defined by $\rho_{nl}(r)=P_{nl}(r)^2$, $\tilde{\varepsilon}_{xc}$ is the exchange and correlation energy per particle in the local approximation, and

$$\begin{aligned}I_{nl}^L(q)=&\int_0^\infty dr\int_0^\infty dr'[\tilde{S}(q;\bar{r}_s^*)-\tilde{S}(q;\bar{r}_s)]\rho_{nl}(r)\\&\times j_L(qr)\rho_{nl}(r')j_L(qr') \ .\end{aligned} \tag{3.13}$$

The first term in Eq. (3.11) represents the total energy as the sum of all the occupied level energies. The rest of the terms in $E_0$ account for the double-counting correction due to the mutual interactions between electrons. The second term in Eq. (3.11) is the correction to the Hartree contribution. This is an exact expression. The next term corresponds to the correction to the local exchange and correlation contribution. An expression similar to that in LDA is employed for it. This term can be calculated easily if $\tilde{\varepsilon}_{xc}$ is known. Since it is rather involved, the actual process to obtain $\tilde{\varepsilon}_{xc}$ from $\tilde{\mu}_{xc}$ will be shown later. The correction to the nonlocal contribution is given in both the last term in Eq. (3.11) and $E_0^{(2)}$ in Eq. (3.12). In the derivation of the former, the $r_s$ value is fixed to $\bar{r}_s$ in $\tilde{\varepsilon}(q;r_s)$ and the factor $\frac{1}{2}$ is used by the assumption that the deviation from the usual Fock correction is small. In this sense, $E_0^{(1)}$ may be regarded as the total energy in the fixed-$\bar{r}_s$ approximation. The correction due to the change in $r_s$ is provided in $E_0^{(2)}$, in which only leading terms are taken into account.

Now we show our process to determine $\tilde{\varepsilon}_{xc}$ from $\tilde{\mu}_{xc}$. If we divide $\tilde{\varepsilon}_{xc}$ into the correlation and the exchange parts as

$$\tilde{\varepsilon}_{xc}[r_s]=\varepsilon_c[r_s]+\tilde{\varepsilon}_x[r_s] \ , \tag{3.14}$$

$\varepsilon_c$ is a known quantity, given by the interpolation expression of Vosko, Wilk, and Nusair [20]. On the other hand, the local exchange energy $\tilde{\varepsilon}_x$ is not known. This must be derived from the corresponding local exchange contribution to the chemical potential, $\tilde{\mu}_x$, in Eq. (2.10). For this purpose, we note a theorem due to Seitz [28] which relates the ground-state energy to the chemical potential as

$$\tilde{\mu}_x[r_s]=\tilde{\varepsilon}_x[r_s]-\frac{r_s}{3}\frac{d\tilde{\varepsilon}_x[r_s]}{dr_s} \ . \tag{3.15}$$

By solving this differential equation numerically, we can obtain $\tilde{\varepsilon}_x$ from $\tilde{\mu}_x$. After an inspection of the obtained results, we find that $\tilde{\varepsilon}_x$ can be written as

$$\tilde{\varepsilon}_x[r_s]=\tilde{\mu}_x[r_s^*] , \qquad (3.16)$$

where the scaled $r_s$ parameter, $r_s^*=\zeta r_s$, is introduced with the scaling factor $\zeta=1.3698$. This value of $\zeta$ is associated with LFF in Eq. (2.5) and it is independent of $r_s$ in a very wide range of $r_s$. This indicates that LFF, which is a source for the $r_s$ dependence, has no influence on the functional form of $r_s$ in the local exchange potential. In the case of the usual exchange potential $\mu_x$, which is inversely proportional to $r_s$, $\zeta$ is obtained analytically as $\zeta=\frac{4}{3}$, which is very close to our value of $\zeta$.

The inclusion of the $\eta$ parameter is self-evident: The change indicated in Eq. (2.13) should be done. So we will not give the modification introduced by $\eta$ explicitly here.

## IV. RESULTS

### A. Local-field factor

Basically, the values of $G(z)$ at both $z=0$ and $\infty$ are, respectively, determined by the compressibility sum rule and the pair distribution function at zero separation. In the intermediate values of $z$, no such guiding principles exist and thus $G(z)$ is not determined uniquely. Fortunately, however, the eigenenergies in Eq. (3.2) as well as the total energy are virtually independent of the choice of $G(z)$ provided that $G(z)$ near $z=0$ has a correct value. To prove this statement, we have tried with LFF as

$$G_{\mathrm{SOY}}(z)\equiv G(z)+[0.6-G(1)]e^{-(z-1)^2/0.7} , \qquad (4.1)$$

in addition to the calculation with $G(z)$ in Eq. (2.5). The function (4.1) successfully reproduces LFF proposed by Suehiro, Ousaka, and Yasuhara (SOY) [29] which has a peak structure in the vicinity of $z=1$ to mimic the effect due to the nonlocal exchange potential by a local one. If we compare the results employing $G_{\mathrm{SOY}}(z)$ with those using $G(z)$, the difference in the total energy is negligibly small: In the closed-shell atoms such as Be, Ne, Mg, and Ar, the deviations are, respectively, given as 0.03%, 0.02%, 0.03%, and 0.05%. The same is true for the level energies. This conclusion does not change at all even if we try other possible forms for LFF.

### B. Total energy

The calculated results for the total energy with $\eta=0$ and 1 are, respectively, given in the columns HF+C and CHF in Table I for the neutral atoms in the Periodic Table from He to Ca. We did not calculate $E_0$ for atoms beyond Ca, because the corrections due to the relativistic effect [30] cannot be neglected in those atoms. In all the atoms treated here, the contribution $E_0^{(1)}$ in Eq. (3.11) dominates over $E_0^{(2)}$ in Eq. (3.12) in CHF: Generally, the latter gives a correction of the order of 0.01 in atomic units to the former. The total energies of the HF+C have previously been reported in detail by Carroll, Bader, and Vosko [12] with various choices for the correlation potential in the local spin-density approximation. As noted previously, the correlation energies are evaluated with the electronic densities in HF in their treatment. This means that they did not complete the self-consistent calculation. Our total energies of the HF+C in Table I, on the other hand, are the results in the full self-consistent calculation. We find that this self-consistent procedure does not give any significant change. Thus the charge density in HF is actually very close to the self-consistent charge density.

Our present results are compared with the experimental results [31] as well as those in LDA and HF which are

TABLE I. Total energies of neutral atoms ($-E_0$ in a.u.).

| | Experiment[a] | LDA | HF | HF+C<br>$\eta=0$ | CHF<br>$\eta=1$ | $\eta$-CHF<br>$\eta=2/3$ |
|---|---|---|---|---|---|---|
| He | 2.904 | 2.835 | 2.862 | 2.975 | 2.856 | 2.896 |
| Li | 7.478 | 7.335 | 7.433 | 7.595 | 7.398 | 7.464 |
| Be | 14.667 | 14.447 | 14.573 | 14.798 | 14.532 | 14.620 |
| B | 24.653 | 24.344 | 24.529 | 24.825 | 24.494 | 24.594 |
| C | 37.844 | 37.426 | 37.689 | 38.064 | 37.676 | 37.795 |
| N | 54.587 | 54.025 | 54.401 | 54.863 | 54.425 | 54.559 |
| O | 75.063 | 74.473 | 74.809 | 75.361 | 74.888 | 75.033 |
| F | 99.725 | 99.100 | 99.409 | 100.056 | 99.556 | 99.710 |
| Ne | 128.928 | 128.233 | 128.547 | 129.294 | 128.773 | 128.932 |
| Na | 162.245 | 161.440 | 161.859 | 162.674 | 162.041 | 162.254 |
| Mg | 200.043 | 199.139 | 199.615 | 200.507 | 199.796 | 200.032 |
| Al | 242.336 | 241.316 | 241.877 | 242.848 | 242.059 | 242.322 |
| Si | 289.348 | 288.197 | 288.854 | 289.911 | 289.052 | 289.338 |
| P | 341.240 | 339.946 | 340.719 | 341.865 | 340.942 | 341.249 |
| S | 398.100 | 396.716 | 397.505 | 398.742 | 397.770 | 398.093 |
| Cl | 460.149 | 458.664 | 459.482 | 460.815 | 459.738 | 460.096 |
| Ar | 527.549 | 525.946 | 526.817 | 528.249 | 527.112 | 527.490 |
| K | | 598.197 | 599.165 | 600.668 | 599.446 | 599.852 |
| Ca | | 675.742 | 676.758 | 678.341 | 677.047 | 677.477 |

[a] Reference [31].

given in the columns indicated by Experiment, LDA, and HF in Table I. (Data for K and Ca are not available to us.) Note that the results in LDA are obtained using the expression of Vosko, Wilk, and Nusair for the local exchange-correlation potential. We find such a general trend as

$$E_0(\mathrm{LDA}) > E_0(\mathrm{HF}) > E_0(\mathrm{experiment}) > E_0(\mathrm{HF+C}) \ . \tag{4.2}$$

The results in CHF are located between LDA and HF for atoms lighter than N, while they are between HF and experiment otherwise. In either case, the correlation energies are underestimated in CHF.

Since the experimental results always lie between the results with $\eta=0$ (corresponding to HF+C) and $\eta=1$ (to CHF), we can naturally expect a perfect fit to experiment by a suitable choice of $\eta$. In Fig. 1, the calculated results of $E_0$ with the change of $\eta$ are shown for such neutral atoms as Be, B, C, N, and Ne by the solid circles, solid squares, solid diamonds, solid triangles, and open squares, respectively. In order to give all the results in one figure, we plot the deviation from the experimental results instead of the values for $E_0$ themselves. A remarkable point is that for each atom, $E_0$ has a linear dependence on $\eta$. In addition, the calculated $E_0$ is found to reproduce the experimental value for $\eta$ around $\frac{2}{3}$, irrespective of the kind of atoms.

In order to investigate the above point in more detail, we have determined the value for $\eta, \eta_0$, which yields $E_0$ in perfect agreement with the experimental value. The values of $\eta_0$ are plotted in Fig. 2 as a function of the atomic number $Z$. Although it is less than 0.6 for $Z \leq 6$, $\eta_0$ is always close to $\frac{2}{3}$ for $Z > 6$. Thus we propose to perform CHF with $\eta=\frac{2}{3}$ for an *ab initio* calculation of the ground-state properties in inhomogeneous electron systems. A trial along this line is given in the column $\eta$-CHF with $\eta=\frac{2}{3}$ in Table I for $E_0$ of atoms. Notice that $E_0$ thus obtained is in good agreement with experiment with accuracy of 0.08% or less.

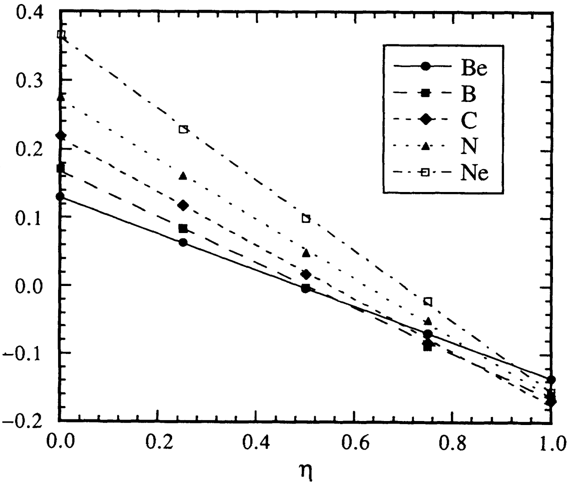

FIG. 1. Calculated total energies of neutral atoms as a function of $\eta$ in the $\eta$-CHF method. Deviation from the experimental value is shown for each atom. The results for Be, B, C, N, and Ne are, respectively, given by the solid circles, solid squares, solid diamonds, solid triangles, and open squares. Those calculated points are interconnected by the lines for a guide to the eyes.

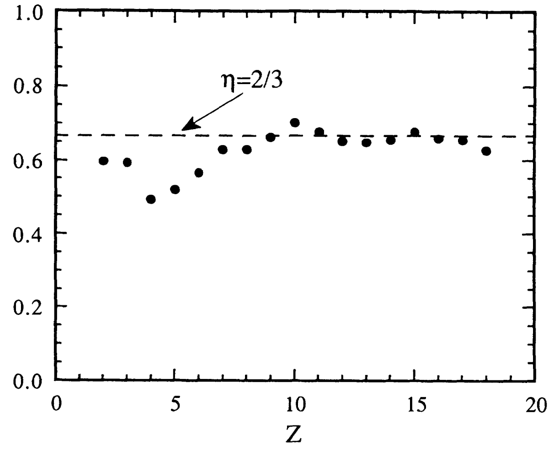

FIG. 2. Values of $\eta_0$ for atoms with the atomic number $Z$ from 2 to 20. Note that $\eta_0$ is the value which reproduces the experimental result of $E_0$ in the $\eta$-CHF method.

### C. First ionization potentials

The ionization potential (IP) is defined as the difference between the ground-state energy of a neutral atom and that of the corresponding ion in which some electrons are removed from the atom. In particular, the smallest energy to extract an electron from the neutral atom is called the first ionization potential (FIP), $I_1$. The results for $I_1$ in our $\eta$-CHF with $\eta=\frac{2}{3}$ are given in Fig. 3 by the solid circles. For comparison, the experimental values are shown by the solid squares. The agreement is good in all the atoms treated here. The relative error is at most 5%.

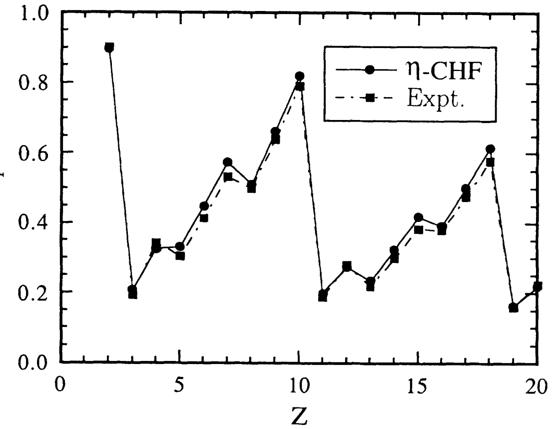

FIG. 3. First ionization potentials as a function of the atomic number. The solid circles and squares represent, respectively, the result in $\eta$-CHF with $\eta=\frac{2}{3}$ and experimental ones given in Ref. [32]. Note that the present values in the $\eta$-CHF method are regarded as the ones in the relaxed scheme.

### D. Effect of relaxation

In estimating IP, we often assume Koopmans's theorem, which asserts that IP is directly connected to the sum of energies for the levels being unoccupied by the ionization process. The value of IP estimated in this way is usually called the unrelaxed IP. In this context, the value in the preceding subsection may be denoted by the relaxed IP. The word "unrelaxed" refers to the fact that the theorem holds only if the wave function for each occupied energy level in the ion is not relaxed, i.e., remains the same as that in the atom.

In Fig. 4, we show the calculated results for unrelaxed $I_1$ which is equal to the negative energy of the highest occupied state, $I_1 = -\varepsilon_{\max}$. As in Table I, the results in LDA, HF, HF+C, and CHF are given with the experimental results. From a fundamental point of view, the level energies in LDA are not physical ones but introduced only as a means to yield a correct electron density. Nonetheless, $I_1$ has been estimated by use of the level energy in LDA or its modified methods. In the unrelaxed picture, we have such a trend as

$$I_1(\text{LDA}) < I_1(\text{CHF}) < I_1(\text{experiment}) < I_1(\text{HF}) < I_1(\text{HF+C}) \,. \tag{4.3}$$

This relation holds except for Be, Mg, and Al in which the order between $I_1$(experiment) and $I_1$(HF) reverses. Compared to Fig. 3, the agreement between experiment and theory becomes worse. Even if we employ $\eta$-CHF with $\eta=\frac{2}{3}$, the agreement is not good in the unrelaxed calculation. In this respect, the effect of the relaxation is crucial to obtain a quantitative agreement. Qualitatively, we can observe that the experimental $I_1$ as well as the relaxed $\eta$-CHF value show a local minimum at O and S. Such a local minimum in $I_1$ cannot be reproduced in any unrelaxed calculation including $\eta$-CHF. This local minimum is due to the Hund coupling connected with

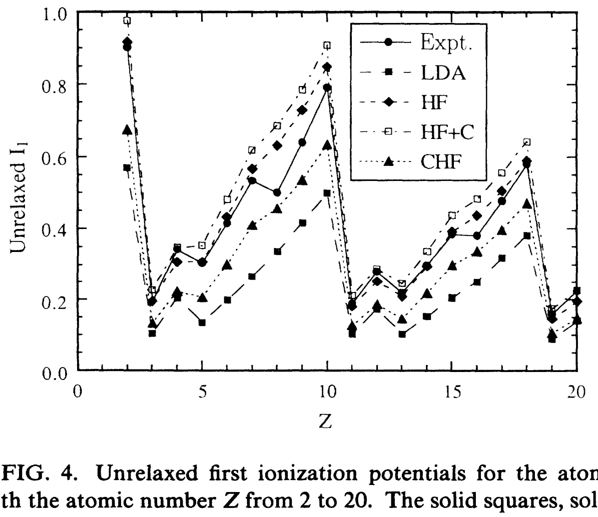

FIG. 4. Unrelaxed first ionization potentials for the atoms with the atomic number Z from 2 to 20. The solid squares, solid diamonds, open squares, and solid triangles correspond to the calculated results in LDA, HF, HF+C, and CHF, respectively. Those results are compared with the experimental ones given by the solid circles.

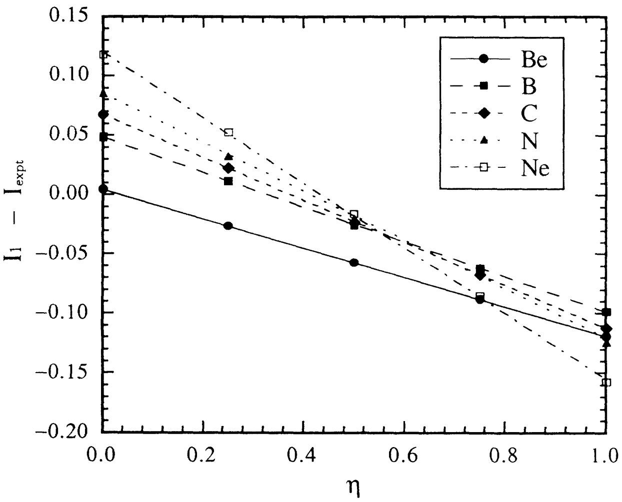

FIG. 5. Calculated results for the first ionization potential minus the experimental value as a function of $\eta$ in the $\eta$-CHF method for Be, B, C, N, and Ne shown by the solid circles, solid squares, solid diamonds, solid triangles, and open squares, respectively.

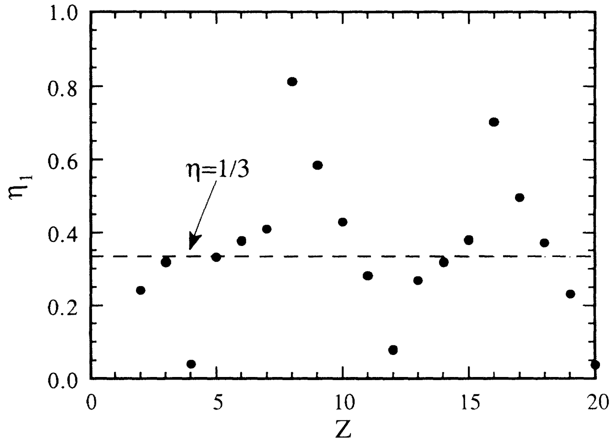

FIG. 6. Values of $\eta_1$ for the atoms with the atomic number $Z$ from 2 to 20. At this value of $\eta_1$, we can reproduce the experimental first ionization potential in the $\eta$-CHF method with the unrelaxed scheme.

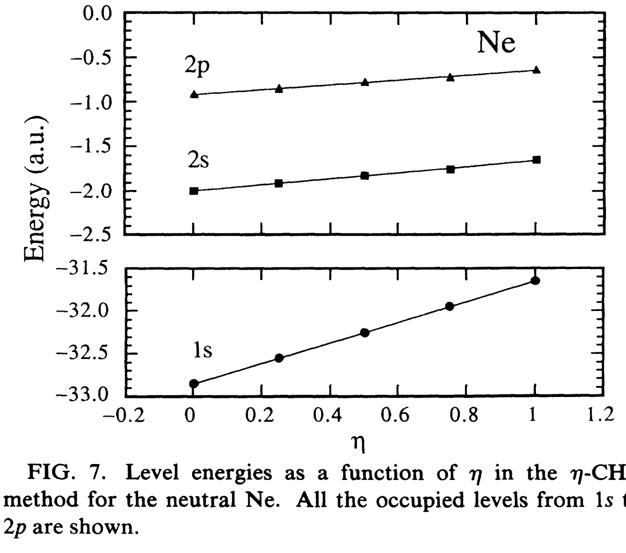

FIG. 7. Level energies as a function of $\eta$ in the $\eta$-CHF method for the neutral Ne. All the occupied levels from 1$s$ to 2$p$ are shown.

TABLE II. Energy levels in the ground states for Ne (a.u).

| | LDA | HF | HF+C | CHF | Experiment[a] |
|---|---|---|---|---|---|
| 1*s* | −30.306 | −32.772 | −32.847 | −31.644 | −32.0 |
| 2*s* | −1.323 | −1.930 | −1.992 | −1.649 | −1.78 |
| 2*p* | −0.498 | −0.850 | −0.910 | −0.635 | −0.80 |

[a] Reference [33].

the *LS* term: In the unrelaxed calculation, only the state with $^3P$ is treated, while in the relaxed calculation, the difference of the energies between the state with $^3P$ and that with $^4S$ is considered.

As shown in (4.3), the experimental $I_1$ is sandwiched between the values in HF+C with $\eta=0$ and CHF with $\eta=1$. This indicates that the relaxation effect might be accounted for by the change of $\eta$ from the value $\frac{2}{3}$. In order to check this idea in more detail, we plot the results for $I_1-I_{\text{expt}}$ in the unrelaxed scheme in Fig. 5 for Be, B, C, N, and Ne by the solid circles, solid squares, solid diamonds, solid triangles, and open squares, respectively, where $I_{\text{expt}}$ is the experimental value of FIP. As in Fig. 1, we find again the linear dependence of $I_1$ on $\eta$. Thus we can easily determine the value of $\eta, \eta_1$, at which $I_{\text{expt}}$ is reproduced. In Fig. 6, the results for $\eta_1$ are plotted as a function of the atomic number *Z*. The average value for $\eta_1$ is $\frac{1}{3}$ which should be compared with $\eta_0=\frac{2}{3}$. The reason why $\eta_1$ is reduced from $\eta_0$ may be explained as follows: In the relaxed calculation, the wave functions for the occupied levels shrink from those in the unrelaxed calculation. A shrink in real space implies an expansion in momentum space. This means that large-*q* scattering processes which are less screened than small-*q* ones become more important in the relaxed case. Thus, even if we employ $\eta_0$ as large as $\frac{2}{3}$, the effect of screening is not large compared to the unrelaxed case. The present calculation shows that such a reduction in the screening effect with the shrunken, i.e., relaxed, wave functions is accounted for by the reduction of $\eta$ in the unrelaxed calculation. Note, however, that the evaluation of $I_1$ with $\eta=\frac{1}{3}$ has generally a rather large error, because $\eta_1$ in Fig. 6 scatters in a quite wider range than $\eta_0$ in Fig. 2.

### E. Energy levels

So far, only the highest occupied level is considered. In order to investigate the behavior of deeper levels, we give all the level energies in Tables II and III for neutral Ne and Ar atoms, respectively. Similar to (4.3), we find the following relation for all occupied levels:

$$\varepsilon_i(\text{LDA}) > \varepsilon_i(\text{CHF}) > \varepsilon_i(\text{experiment}) > \varepsilon_i(\text{HF}) > \varepsilon_i(\text{HF+C}) \ . \qquad (4.4)$$

Once again, the experimental value is always sandwiched by the values at $\eta=0$ and 1. In Fig. 7, $\varepsilon_i$ is drawn as a function of $\eta$ for Ne. We find that all the levels behave in a quite similar way: They change in proportion to $\eta$. At first sight, this is a very curious behavior. With the change of the screening effect introduced by the change of $\eta$, the wave function at each level is expected to behave differently, depending on the site where it is located. Then such a different behavior in the wave function with $\eta$ will be reflected in $\varepsilon_i$, but actually this is not the case. This indicates that the change in the wave function due to the alternation of $\eta$ is negligibly small. Thus we may conclude that the wave function itself is already given rather accurately in HF.

## V. SUMMARY AND FUTURE PROBLEMS

In this paper, we have proposed an improvement on the correlated Hartree-Fock calculation of the ground-state energies $E_0$ as well as the first ionization potentials $I_1$ for atoms by the introduction of the $\eta$ parameter. The optimum value for $\eta$ is determined to be $\frac{2}{3}$. This provides very accurate results for both $E_0$ and $I_1$. The effect of relaxation during the ionization process may be included by the choice of $\eta=\frac{1}{3}$ in the calculation for the level energies in the unrelaxed scheme, though $I_1$ thus obtained is not always very accurate.

At present, we do not see any reason why the present $\eta$-CHF method does not give results for molecules, insulators, and semiconductors with the same accuracy as for atoms. Thus the application to those systems is one of our future problems. For the metals, however, we do not know whether the same $\eta=\frac{2}{3}$ remains the best choice or

TABLE III. Energy levels in the ground states for Ar (a.u.).

| | LDA | HF | HF+C | CHF | Experiment[a] |
|---|---|---|---|---|---|
| 1*s* | −113.800 | −118.610 | −118.697 | −116.833 | −118.1 |
| 2*s* | −10.794 | −12.322 | −12.388 | −11.681 | −12.1 |
| 2*p* | −8.443 | −9.571 | −9.639 | −8.953 | −9.25 |
| 3*s* | −0.883 | −1.277 | −1.332 | −1.094 | −1.08 |
| 3*p* | −0.382 | −0.591 | −0.643 | −0.471 | −0.58 |

[a] Reference [33].

not, because the screening may work in a much different way for the conduction bands in metals. Thus this constitutes another future problem.

## ACKNOWLEDGMENT

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## APPENDIX: LOCAL-FIELD FACTOR AND LOCAL EXCHANGE POTENTIAL

In Ref. [19], the parameters $A$ and $B$ introduced in Eq. (2.5) are, respectively, given as

$$A=\frac{1}{4}+0.019\,18\lambda^2\frac{(1+a_1\lambda)^2+\frac{4}{3}a_2\lambda^2(1+\frac{7}{8}a_1\lambda)+\frac{3}{2}a_3\lambda^3(1+\frac{8}{9}a_1\lambda)}{(1+a_1\lambda+a_2\lambda^2+a_3\lambda^3)^2}\,, \tag{A1}$$

with $a_1=12.05$, $a_2=4.254$, and $a_3=1.363$ and

$$B=\frac{3A}{2-(1+\frac{1}{2}\lambda^2+\frac{1}{12}\lambda^4+\frac{1}{144}\lambda^6+\frac{1}{2400}\lambda^8)^{-2}}\,, \tag{A2}$$

where the parameter $\lambda$ was defined in Eq. (2.7). With the choice of the local-field factor in Eq. (2.5), $\tilde{\mu}_x$ in Eq. (2.10) is calculated in units of Ry as

$$\tilde{\mu}_x=-\frac{1.216}{\lambda}\frac{1+0.2307\lambda}{1+1.532\lambda+0.4291\lambda^2}\,. \tag{A3}$$

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