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# Soft Coulomb hole for the Hartree-Fock model to estimate atomic correlation energies

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An empirical model for the correlation energy ($E_c$) of atoms is proposed. The method, a perturbation applied to the Roothaan Hartree-Fock atomic functions, requires the reevaluation of the two-electron integrals due to the introduction of a "soft" Coulomb hole whose magnitude is calibrated semiempirically. We have tested it by computing the total correlation energy, the first ionization potentials for atoms helium through xenon, by considering excited states of the ground-state configuration for $Z = 3$ to $Z = 18$ and the electron affinity for fluorine, chlorine, bromine, and iodine ions.

## I. INTRODUCTION

The difficulties in obtaining reliable estimates of correlation energy for electronic systems are well known.[1] Despite the fact that one knows in principle the solution to the problem, the accurate estimation of correlation energy ($E_c$) remains a most stubborn bottleneck. The numerous approaches dealing with the computation of $E_c$ may be naively classified into two broad categories: *ab initio* and semiempirical. The former class of methods consists of variational and nonvariational methods,[1] e.g., configuration-interaction (CI), multiconfiguration self-consistent-field method (MCSCF), many-body perturbation theoretical methods (MBPT's), electron-pair theories, density-matrix methods, etc. All these methods are numerically intensive and require vast amounts of computer time to obtain accurate estimates of correlation energy. Moreover, these methods exhibit limitations for large systems with more than one or two dozen electrons. Hence it is advisable to resort, for some time, to parametric theories, statistical models, and semiempirical methods. In our opinion, since the Coulomb hole and $E_c$ is defined with reference to a Hartree-Fock (HF) wave function, it is most reasonable to start with HF quality functions before meaningfully attempting to introduce a term which approximates Coulomb correlation.

In the present work an empirical parametric perturbation term to the HF total energy is developed for atoms. A number of checks to the constituents of the total correlation energy are provided; specifically, ionization potentials,[2] total correlation energies,[3] and the corresponding pair correlation energies[4] have been computed. The computational time remains essentially as modest as for the HF model.

## II. THEORETICAL BACKGROUND

Electron correlation is of two kinds: the Fermi hole in which electrons of parallel spin are kept apart, and the Coulomb hole in which electrons of opposite spin are kept apart. As is well known, electrons of parallel spin are correlated via the antisymmetry principle leading to the exchange term in the HF model. However, the HF model clearly ignores the Coulomb hole correlation. This means that the conditional probability density of electron 1 and electron 2 with opposite spin being at the same site is not zero but finite for the HF model. There have been a number of studies attempting to graft a Coulomb hole onto the HF model. One of the earliest is Wigner's[5] proposal of a local density-functional correction for an electron gas of low density. This study and the development of density-functional theory led to a number of local and nonlocal density-functional models for correlation energy.[6] We recall that the local density-functional models are based on the assumption that the functional derivative of $E_c$ with respect to density is mainly a function of electron density at that point rather than its gradients or integrals.

Following Wigner, Gombas[7] gave a combined expression for the correlation energy which covered both high- and low-density regions. Clementi[3] fitted the form proposed originally by Wigner to the $E_c$ of various atoms. This functional was suitably adapted and also worked reasonably well for molecules as has been shown by Lie and Clementi.[8] Among the electron gas models a recent one[9] parametrizes the results of Ceperley and Alder.[10] Colle and Salvetti[11] derived an approximate expression for $E_c$ by modeling the first- and second-order density matrices. Their model has been employed satisfactorily in the studies of small molecules such as ethylene, formaldehyde,[11] and also to derive an interaction potential for liquid water.[12] Among the nonlocal models for $E_c$ we recall, for example, the functionals of Langreth and coworkers,[13] Gunnarson *et al.*,[14] and Alonso and Balbas.[15] However, due to the form of the correction prescribed in some of these theories,[14,15] requiring the normalization of the exchange correlation hole at every step of the self-consistent-field (SCF) process, such functionals are computationally somewhat complicated. Although some of the electron-density-based models for $E_c$ provide a simpler alternative to accurate atomic wave-mechanical prescriptions such as configuration interaction (CI) and MCSCF, in general, the density-functional methods become rather impractical in molecular computations, since one has to deal with integrals of fractional powers of the density, often requiring numerical integrations. Recently, Fuentealba *et al.*[16] have presented an empirical polarization potential for the study of $E_c$ of atoms with up to four electrons.

In light of the recent developments and to provide a sufficient basis for our study, an earlier model[17] for the Coulomb hole in atoms is presented in detail below.

## III. HARD AND SOFT COULOMB HOLES

It is instructive to recall that there are several schemes for the HF method leading to somewhat different energies and consequently to different values of correlation energy. In this study, when we refer to the Hartree-Fock energy, we mean the best energy one can obtain by employing the spin-restricted analytical self-consistent-field method as put forward by Roothaan.[18] The total energy within the Roothaan Hartree-Fock (RHF) method is written as

$$\begin{aligned} E = {} & 2\sum_k H_k + \sum_{k,l}(2J_{kl}-K_{kl}) \\ & + f\left[2\sum_m H_m + f\sum_{m,n}(2aJ_{mn}-bK_{mn}) \right. \\ & \left. + 2\sum_{k,m}(2J_{km}-K_{km})\right] . \end{aligned} \tag{1}$$

Here, in referring to the individual orbitals, indices $k$ and $l$ are used for the closed-shell orbitals and $m$ and $n$ are for the open-shell orbitals. The numerical constants $a$, $b$, and $f$ depend on the specific $LS$-coupling state of an atom and its configuration.

Symmetry considerations and linear combination of atomic orbitals (LCAO) form of Roothaan's open-shell SCF theory require the evaluation of the following integrals:

$$\begin{aligned} J_{\lambda pq,\mu rs} = (d_\lambda d_\mu)^{-1} \sum_{\alpha,\beta} \int\int \chi^*_{p\lambda\alpha}(1)\chi_{q\lambda\alpha}(1)\left[\frac{1}{r_{12}}\right]\chi^*_{r\mu\beta}(2) \\ \times \chi_{s\mu\beta}(2)d\mathbf{r}_1 d\mathbf{r}_2 , \end{aligned} \tag{2a}$$

$$\begin{aligned} K_{\lambda pq,\mu rs} = (d_\lambda d_\mu)^{-1} \sum_{\alpha,\beta} \int\int \chi^*_{p\lambda\alpha}(1)\chi_{s\mu\beta}(1)\left[\frac{1}{r_{12}}\right]\chi^*_{r\mu\beta}(2) \\ \times \chi_{q\lambda\alpha}(2)d\mathbf{r}_1 d\mathbf{r}_2 , \end{aligned} \tag{2b}$$

where the symmetry basis functions $\chi_{p\lambda\alpha}$ denote the $p$th basis function of species $\lambda$ and subspecies $\alpha$ and $d_\lambda$ is the dimension of the representation $\lambda$. Clementi[17] proposed to correct for the electrons with antiparallel spins by introducing a hole around each electron and not allowing these holes to be superimposed; this technique is named the Coulomb-Hartree-Fock (CHF) method. Let us now briefly comment on the CHF technique[17] since this is also a starting point for our investigation. For simplicity the hole was assumed to be a spherical well centered around the electron; in this way a "hard" hole was grafted onto RHF equations. A main concern was to refrain from increasing the numerical as well as mathematical complexity of the problem beyond the RHF formalism. The hard Coulomb hole was introduced directly as a modification of the Coulomb integral in Eq. (2a) replacing the usual integration range,[19]

$$\int_0^\infty f(1)\left[\int_0^{r_1} f'(2)dr_2 + \int_{r_1}^\infty f''(2)dr_2\right]dr_1 \tag{3}$$

into

$$\int_0^\infty f(1)\left[\int_0^{r_1-\delta} f'(2)dr_2 + \int_{r_1+\delta}^\infty f''(2)dr_2\right]dr_2 . \tag{4}$$

Here $f(1)$, $f'(2)$, and $f''(2)$ are functions of electrons 1 and 2 after integration over the solid angle. For a complete expression see, for example, Ref. 19. Since in the integration limit of $r_2$ in Eq. (3) the two electrons occupy the same radial position, the effect of replacing $r_1$ by $r_1-\delta$ and $r_1+\delta$ introduces a discontinuity in the potential, thus introducing a Coulomb hole. We recall that a suitable expression was obtained for $\delta_{\lambda pq,\mu rs}$ in terms of the constituent Slater-type orbitals (STO's) $\chi_{\lambda p}$, $\chi_{\lambda q}$, $\chi_{\mu r}$, and $\chi_{\mu s}$:

$$\begin{aligned} \delta_{\lambda pq,\lambda rs} = \frac{c_1}{16}\left[\left[\frac{n_p}{\zeta_p^2}+\frac{n_q}{\zeta_q^2}\right]S_{pq} + \left[\frac{n_r}{\zeta_r^2}+\frac{n_s}{\zeta_s^2}\right]S_{rs}\right] \\ \times (S_{pr}+S_{ps}+S_{qr}+S_{qs}) \end{aligned} \tag{5a}$$

and

$$\begin{aligned} \delta_{\lambda pq,\mu rs} = \frac{c_1}{24c_2}\left[\left[\frac{n_p}{\zeta_p^2}+\frac{n_q}{\zeta_q^2}\right]S_{pq}^2 + \left[\frac{n_r}{\zeta_r^2}+\frac{n_s}{\zeta_s^2}\right]S_{rs}^2\right] \\ \times (S_{pr}^2+S_{ps}^2+S_{qr}^2+S_{qs}^2) \end{aligned} \tag{5b}$$

for $\lambda \neq \mu$. Here $n_p$ denotes the principal quantum number of the STO, $\zeta_p$ is the orbital exponent, and $S_{pq}$ is the "radial overlap" of the two STO's:

$$S_{pq} = \frac{(n_p+n_q+1)!}{[\frac{1}{2}(\zeta_p+\zeta_q)]^{n_p+n_q+1}}\left[\frac{\zeta_p^{2n_p+1}\zeta_q^{2n_q+1}}{(2n_p+1)!(2n_q+1)!}\right]^{1/2} . \tag{6}$$

The parameters $c_1 = 0.028\,816$ and $c_2 = 1.1$ had been obtained by fitting the $E_c$ for the helium and neon atoms. This functional expression had been obtained with numerical experimentation and modeling and has served well in yielding at least as reliable estimates of $E_c$ as any other currently available method. However, there are serious shortcomings of the model: (1) it may be applied only to atoms and with a STO basis set, (2) the form of the correction (cutting the Coulomb integral with a hard hole) introduces a discontinuity in the effective potential, and (3) only $s$ and $p$ electrons were considered, thus limiting the model's usefulness. All the above drawbacks are eliminated in the "soft" Coulomb hole model presented below.

The evident inadequacy of the two-electron conditional probability density distribution within HF theory to obey limiting conditions at small $|\mathbf{r}_1-\mathbf{r}_2|$ can be corrected by constraining the approach of electron 1 to electron 2. In contrast to Eq. (4), here a Coulomb hole is introduced by adding a perturbation term in the effective potential of the form

$$-\frac{e^{-\eta r_{12}^2}}{r_{12}}\ . \tag{7}$$

Here $\eta$ is a parameter determining the magnitude of the Coulomb hole and is to be calibrated. The "corrected" two-electron integrals are rewritten as follows:

$$J'_{\lambda pq,\mu rs}=(d_\lambda d_\mu)^{-1}\sum_{\alpha,\beta}\int\int\chi^*_{p\lambda\alpha}(1)\chi_{q\lambda\alpha}(1)\left[\frac{1-e^{-\eta r_{12}^2}}{r_{12}}\right]\times\chi^*_{r\mu\beta}(2)\chi_{s\mu\beta}(2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{8a}$$

and

$$K'_{\lambda pq,\mu rs}=(d_\lambda d_\mu)^{-1}\sum_{\alpha,\beta}\int\int\chi^*_{p\lambda\alpha}(1)\chi_{s\mu\beta}(1)\left[\frac{1-e^{-\eta r_{12}^2}}{r_{12}}\right]\times\chi^*_{r\mu\beta}(2)\chi_{q\lambda\alpha}(2)d\mathbf{r}_1 d\mathbf{r}_2\ . \tag{8b}$$

Here in Eq. (8) the correcting term $\exp(-\eta r_{12}^2)$ represents a soft hole, which leads to a smooth cutoff for the potential at small interelectronic distances. This choice of a correction term allows an analytic evaluation of the $J$ and $K$ integrals with a Cartesian Gaussian-type orbital (GTO) basis set. Since $\eta$ defines the size of the Coulomb hole, it has been assumed, as before,[17] that $\eta$ should depend on the basis functions $\chi_{p\lambda\alpha}$, $\chi_{q\lambda\alpha}$, $\chi_{r\mu\beta}$, $\chi_{s\mu\beta}$, and $Z$ the atomic number. We have employed the following form in the parametrization:

$$\eta_{\lambda pq,\mu rs}=A_{\lambda\mu}(1+B_{\lambda\mu}Z)C_{\lambda pq}C_{\mu rs}D_{\lambda pq,\mu rs}\ , \tag{9a}$$

$$A_{\lambda\mu}=e_\lambda+e_\mu\ , \tag{9b}$$

$$B_{\lambda\mu}=f_\lambda+f_\mu\ , \tag{9c}$$

$$C_{\lambda pq}=(\zeta_p\zeta_q)^{v_\lambda}S_{pq}^{a_\lambda}\ , \tag{9d}$$

$$D_{\lambda pq,\mu rs}=[\tfrac{1}{3}(\sqrt{S_{pq}S_{rs}}+\sqrt{S_{ps}S_{qr}}+\sqrt{S_{pr}S_{qs}})]^{-1}\ . \tag{9e}$$

Here $\zeta_p$ is the orbital exponent for $\chi_{p\lambda\alpha}$, $S_{pq}$ is given by the expression

$$S_{pq}=\begin{cases}\dfrac{s_{pq}}{\sqrt{s_{pp}s_{qq}}} & \text{for } \lambda=\mu\\ 0 \ \text{ for } \lambda\neq\mu\end{cases} \tag{9f}$$

and $s_{pq}$ is the overlap integral:

$$s_{pq}=\frac{1\times 3\times\cdots\times(2\lambda-1)}{2^{\lambda-1}}\frac{\pi^{3/2}}{(\zeta_p+\zeta_q)^{(2\lambda+1)/2}}\ . \tag{9g}$$

The constants $v_\lambda$, $a_\lambda$, $e_\lambda$, and $f_\lambda$ have been fitted and the optimized values for $s$, $p$, and $d$ orbitals are listed below:

$v_s=0.375$ $a_s=0.25$ $e_s=11.1$ $f_s=0.005$
$v_p=0.325$ $a_p=0.43$ $e_p=9.0$ $f_p=0.004$
$v_d=0.3$ $a_d=0.60$ $e_d=8.75$ $f_d=0.$

These values are given to a few decimal figures only, since the parametrization was careful but not exhaustive.

## IV. FITTING DETAILS

All the 12 parameters, i.e., 4 for each symmetry species, have not been fully optimized; however, they have been obtained by a judicious cyclic relaxation of each of them one or, at maximum, two at a time. For instance, with both $a_s$ and $f_s$ set to zero the correlation energy of the helium isoelectronic series was fitted employing $v_s$ and $e_s$. The parameter $a_s$ was obtained by a fitting of lithium and beryllium atoms. After this $e_s$ was reoptimized to fit all the data considered so far and the ionization potential ($I$). A similar strategy was employed for the $v_p$, $a_p$, and $e_p$ with $f_p=0$, fitting for the neon isoelectronic series and the argon atom $E_c$ and $I$. At this point it is important to mention that we have tried to systematically keep a check on the relative magnitudes of the pair correlation energies ($E^{\rm PC}$). Thus, in our parametrization, we had to satisfy many more constraints than simply obtaining a reasonable value of the total correlation energy. The $E^{\rm PC}$ are obtained with no additional numerical effort and are given by the following equations:

$$E_{ij}^{\rm PC}=\tfrac{1}{2}(D^\dagger_{i\lambda}\Delta P D_{j\mu}-D^\dagger_{i\lambda}\Delta Q D_{j\mu})\ , \tag{10}$$

where

$$D_{i\lambda}=N_{i\lambda}C_{i\lambda}C^\dagger_{i\lambda},\quad \Delta P=P'-P,\quad \Delta Q=Q'-Q\ ,$$

and

$$P'=J'-\tfrac{1}{2}K',\quad Q'=\alpha J'-\tfrac{1}{2}\beta K'\ ,$$

$$P=J-\tfrac{1}{2}K,\quad Q=\alpha J-\tfrac{1}{2}\beta K\ .$$

Here $P'$, $Q'$, $P$, and $Q$ are the supermatrices of Roothaan and $J$, $K$, $J'$, and $K'$ have already been defined in Eqs. (2) and (8), $N_{i\lambda}$ is the occupation number of the $i$th shell of symmetry $\lambda$, and $D_{i\lambda}$ is the $i$th shell density matrix. $\alpha$ and $\beta$ are the vector coupling coefficients denoting the $LS$ state under consideration. The pattern for the relative magnitudes of the pair correlation energy was obtained by comparing the experimental $\Delta E_c$ (defined as

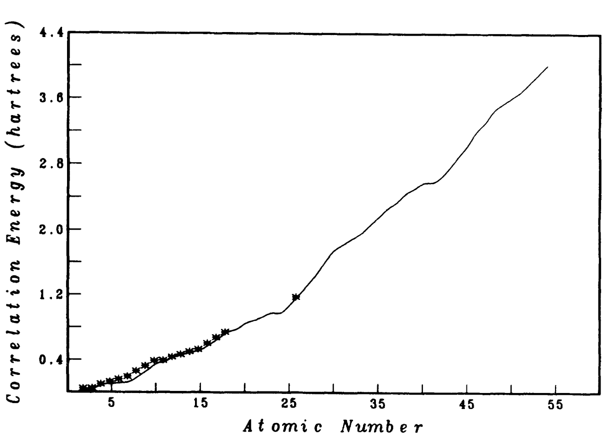

FIG. 1. Correlation energy (hartrees) of neutral atoms plotted against atomic number $Z$ ( $*$, *ab initio* models; ——, computed).

$I_{\rm expt}-I_{\rm HF}$) which is compared with its computed analog ($I_{\rm model}-I_{\rm HF}$). For the parameters $v_d$, $a_d$, and $e_d$ with $f_d=0$ the same strategy has been used. The total correlation energy estimate for iron[20] and the experimental $\Delta E_c$ for atoms with open 3*d* and 4*d* shells have been used for the fitting. In a related paper[21] we give a full tabulation of the $E^{\rm PC}$ for the neutral atoms and singly charged positive ions in their respective ground states.

TABLE I. First ionization potential ($I$) (in eV) of atoms helium through xenon.

| Z | Hartree-Fock | This work | Expt. |
|---|---|---|---|
| 3 | 5.34 | 5.39 | 5.39 |
| 4 | 8.04 | 9.28 | 9.32 |
| 5 | 7.93 | 8.17 | 8.30 |
| 6 | 10.79 | 11.07 | 11.26 |
| 7 | 13.96 | 14.29 | 14.53 |
| 8 | 11.89 | 13.61 | 13.62 |
| 9 | 15.72 | 17.44 | 17.42 |
| 10 | 19.85 | 21.58 | 21.56 |
| 11 | 4.95 | 5.18 | 5.14 |
| 12 | 6.61 | 7.95 | 7.65 |
| 13 | 5.50 | 5.69 | 5.99 |
| 14 | 7.65 | 7.91 | 8.15 |
| 15 | 10.02 | 10.32 | 10.49 |
| 16 | 9.02 | 10.51 | 10.36 |
| 17 | 11.80 | 13.32 | 12.97 |
| 18 | 14.78 | 16.35 | 15.76 |
| 19 | 4.01 | 4.35 | 4.34 |
| 20 | 5.12 | 6.49 | 6.11 |
| 21 | 5.35 | 6.81 | 6.54 |
| 22 | 5.51 | 7.06 | 6.82 |
| 23 | 5.81 | 7.35 | 6.74 |
| 24 | 5.90 | 6.24 | 6.77 |
| 25 | 5.90 | 7.67 | 7.44 |
| 26 | 6.28 | 8.03 | 7.87 |
| 27 | 7.78 | 7.92 | 7.86 |
| 28 | 7.61 | 7.82 | 7.64 |
| 29 | 6.41 | 7.03 | 7.73 |
| 30 | 7.63 | 9.29 | 9.39 |
| 31 | 5.47 | 5.64 | 6.00 |
| 32 | 7.43 | 7.66 | 7.90 |
| 33 | 9.53 | 9.81 | 9.81 |
| 34 | 8.41 | 9.75 | 9.75 |
| 35 | 10.78 | 12.14 | 11.81 |
| 36 | 13.27 | 14.67 | 14.00 |
| 37 | 3.73 | 4.18 | 4.18 |
| 38 | 4.67 | 6.03 | 5.70 |
| 39 | 5.74 | 6.07 | 6.38 |
| 40 | 5.05 | 6.65 | 6.84 |
| 41 | 5.66 | 6.13 | 6.88 |
| 42 | 5.87 | 6.34 | 7.10 |
| 43 | 5.29 | 7.16 | 7.28 |
| 44 | 5.92 | 6.55 | 7.37 |
| 45 | 5.92 | 6.63 | 7.46 |
| 46 | 6.67 | 8.23 | 8.34 |
| 47 | 5.91 | 6.75 | 7.58 |
| 48 | 6.90 | 8.64 | 8.99 |
| 49 | 5.05 | 5.22 | 5.79 |
| 50 | 6.83 | 7.04 | 7.34 |
| 51 | 8.66 | 8.91 | 8.64 |
| 52 | 7.62 | 8.82 | 9.01 |
| 53 | 9.62 | 10.84 | 10.45 |
| 54 | 11.68 | 12.93 | 12.13 |

In the present study, we chose to employ Cartesian Gaussian basis sets; the motivation for this choice is that molecular computations are generally carried out with Cartesian GTO's. This also required the derivation of the familiar Roothaan vector coupling coefficients for ground and excited states of $d^n$ and $sd^n$ configurations. The coupling coefficients for $p^n$ and $sp^n$ have already been provided by Roothaan[18] and Huzinaga.[22] Also, an atomic structure code[23] has been modified[24] to explicitly compute wave functions with Cartesian Gaussian basis sets. In the present study the so-called geometrical basis set[25] has been used for the computation of correlation energy; we recall that in this basis set the orbital exponents are constrained by the relation

$$\zeta_i=\zeta_0 K^{i-1}\,,$$

$\zeta_0$ and $K$ being parameters to be optimized. We have computed the geometrical GTO basis sets for the neutral atoms and singly charged positive ions up to $Z=54$ which yield HF energies that are as accurate as the ones obtained with a STO basis set of Clementi and Roetti.[26]

## V. COMPUTATIONAL TESTS AND DISCUSSION

Figure 1 displays the plot of $E_c$ versus $Z$, the atomic number. The solid curve represents the $E_c$ estimate provided by the present model and the starred points denote the available *ab initio* estimates of $E_c$ in the literature.[3,20] In Fig. 2 the first ionization potentials computed with our method are compared with the HF and experimental values[2] and in Table I the numerical values of the first ionization potentials are tabulated. We stress that we assume that the relativistic corrections to total energy for neutral atoms are equal with their singly charged positive

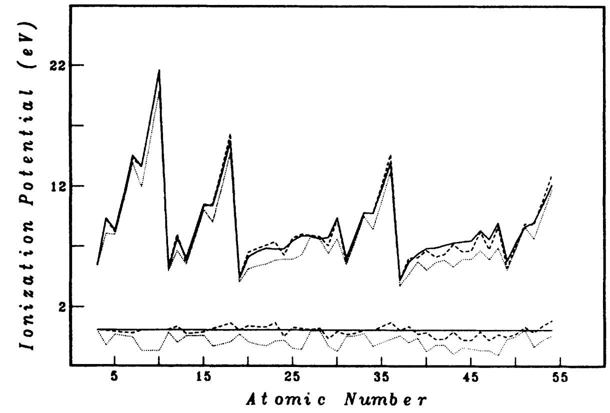

FIG. 2. First ionization potentials (eV) of atoms with $Z=1$–54 (——, experiment; · · · ·, HF; — — —, computed). The corresponding errors in the present model and HF method are also plotted.

ions. Thus the relativistic corrections to the computed first ionization potential are not considered in this study. Clearly this is an approximation which becomes more and more questionable the higher the $Z$ values; thus we felt it to be somewhat unreasonable to pursue any further the optimization of the parameters. The computed $I$ values for atoms with $Z=1$ through $Z=18$ are in good agreement with their experimental ones. Along with the $I$ curves, the error curves for the soft hole model and the HF model are also presented. It may be seen that our errors in the $I$ estimates are discernibly smaller than their HF counterparts.

The $\Delta E_c$ plots (see Fig. 3) are particularly revealing; to start we compare small differences between large numbers, e.g., for argon the energy of the neutral atom is 527.5536 a.u., the energy of the corresponding singly charged positive ion is 526.9527 a.u., and the $\Delta E_c$ which is defined as $I_{\text{model}} - I_{\text{HF}}$ is 0.0578 a.u. In addition, often one or more types of electron pairs are involved in the ionization process, thus not only the total $E_c$ but also the $E^{\text{PC}}$ must be reasonably computed. Finally, we provide data to test the model for a sizable portion of the periodic table. In Fig. 3 the computed $\Delta E_c$ curves for the elements with open $3d$ and $4d$ shells are close to the experimental ones and the irregular trends with $Z$ are nicely reproduced. For the $4p$ and $5p$ the $\Delta E_c$ estimates provided by the present method systematically deteriorate as may be seen from Fig. 3. A rationalization for this behavior may be the neglect of relativistic corrections and the choice of an appropriate coupling scheme.[27] The $\Delta E_c$ curve represents the variation caused in the number of electron pairs after the ionization of the neutral atom to a singly charged positive ion. Take, for example, the $\Delta E_c$ curve for the $2p$ electrons for the oxygen, fluorine, and neon atoms; there is an annihilation of a $p$ pair which is exemplified by the magnitude of $\Delta E_c$. In contrast, for boron, carbon, and nitrogen atoms there is no change in the

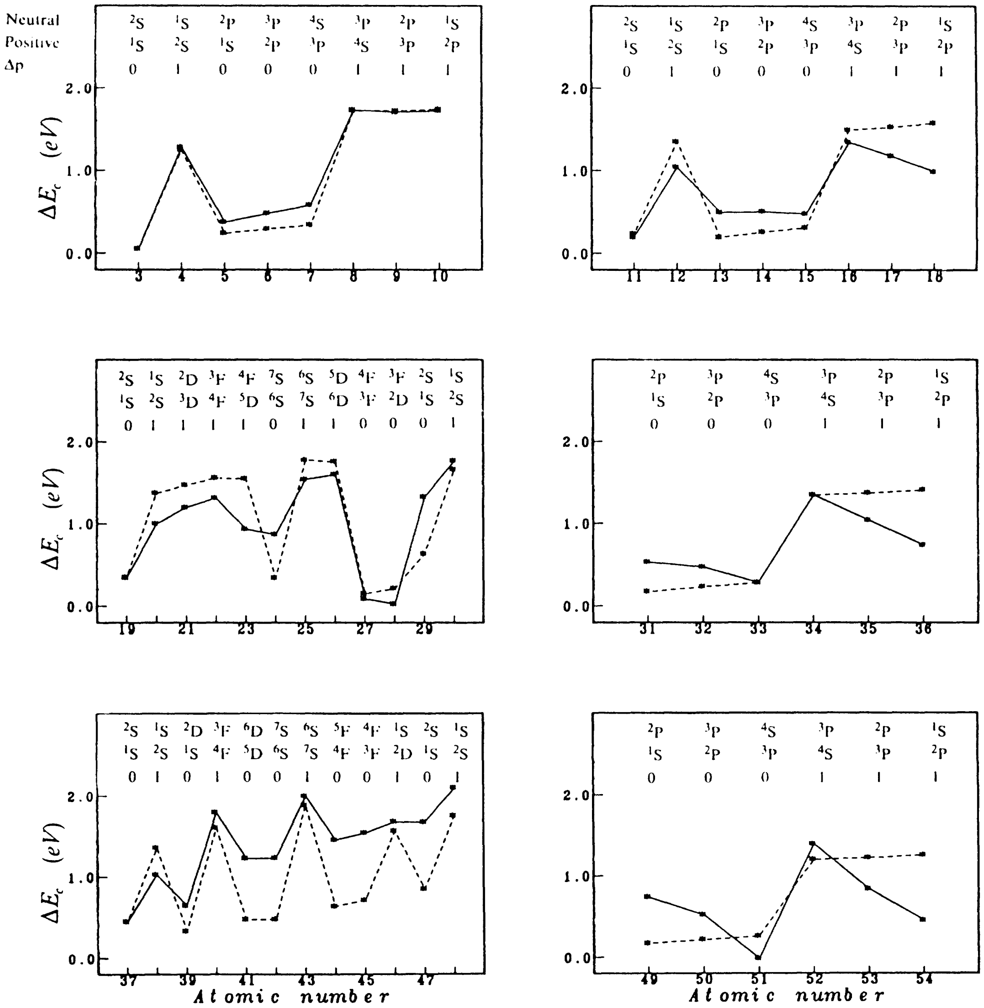

FIG. 3. $\Delta E_c$ (eV) for $ns$, $np$, and $nd$ electrons. The process of neutral atom becoming singly charged positive ion brings about a variation in the number of electron pairs denoted by $\Delta p$ ( * —— *, experiment; * ---- *, computed).

TABLE II. Variation of $E_c$ and HF energies (hartrees) among different basis sets for neon and zinc atoms.

| | | $E_c$ | | HF energy | |
|---|---|---|---|---|---|
| | basis | neutral | positive | neutral | positive |
| Neon | $7s3p$ | 0.3492 | 0.2850 | −128.2849 | −127.1681 |
| | $9s5p$ | 0.3471 | 0.2870 | −128.5282 | −127.3778 |
| | $11s7p$ | 0.3472 | 0.2872 | −128.5452 | −127.3949 |
| | $13s8p$ | 0.3472 | 0.2872 | −128.5465 | −127.3963 |
| | $6s3p$ | 0.3558 | 0.2897 | −127.0534 | −126.0017 |
| | $8s4p$ | 0.3510 | 0.2880 | −128.0965 | −126.9880 |
| | $10s5p$ | 0.3492 | 0.2874 | −128.3936 | −127.2656 |
| | $12s6p$ | 0.3483 | 0.2872 | −128.4894 | −127.3516 |
| | $9s5p$ | 0.3475 | 0.2871 | −128.4647 | −127.3185 |
| | $10s6p$ | 0.3476 | 0.2872 | −128.5281 | −127.3804 |
| | $13s8p$ | 0.3474 | 0.2871 | −128.5440 | −127.3951 |
| | $6s3p$ | 0.3499 | 0.2851 | −127.8098 | −126.6846 |
| | $7s3p$ | 0.3500 | 0.2852 | −128.1774 | −127.0573 |
| | $9s3p$ | 0.3501 | 0.2855 | −128.2903 | −127.1757 |
| | $10s6p$ | 0.3476 | 0.2872 | −128.5281 | −127.3804 |
| | $13s8p$ | 0.3472 | 0.2872 | −128.5466 | −127.3963 |
| Zinc | $14s9p5d$ | 1.7422 | 1.6896 | −1777.7594 | −1777.3996 |
| | $15s7p5d$ | 1.7612 | 1.7109 | −1774.9647 | −1774.6280 |
| | $16s10p7d$ | 1.7402 | 1.6879 | −1777.6099 | −1777.2448 |
| | $19s11p8d$ | 1.7398 | 1.6877 | −1777.8162 | −1777.4506 |

status of number of pairs from neutral to the positive ion and hence, in turn, the $\Delta E_c$ for these cases is comparatively smaller. However, the experimental $\Delta E_c$ curve for $5p$ electrons shows an anomalous trend. It may be seen that the $\Delta E_c$ for indium has almost the same magnitude as $\Delta E_c$ for xenon, in spite of the fact that there is a loss of a $p$ pair, whereas indium loses only a $p$-shell electron. This may perhaps be attributed to a systematic breakdown of the *LS*-coupling scheme; this occurs gradually from $2p$ through $5p$ shells as seen from Fig. 3.

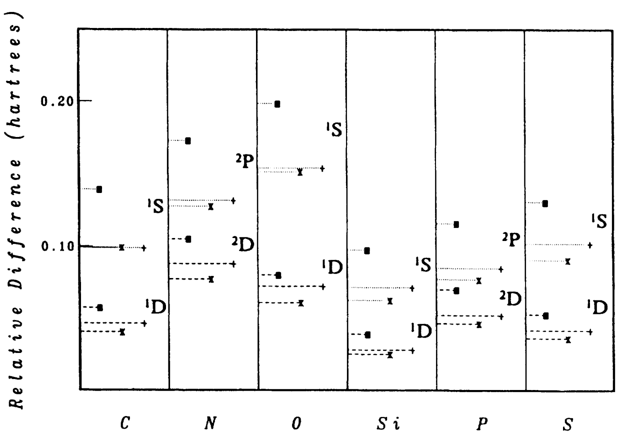

FIG. 4. Relative differences in total energy (hartrees) for excited states with respect to the total energy of the ground-state configuration for neutral atoms with $Z=6$, 7, 8, 14, 15, and 16 (---■, HF; ---*, computed; ---+, experiment).

For the excited states of the ground-state HF configuration, the present functional exhibits a satisfactory discrimination among the magnitudes of $E_c$ estimates of the various states. Moreover, the relative differences between the excited states are satisfactorily reproduced as displayed in Fig. 4 for atoms with $Z=6$, 7, 8, 14, 15, and 16. We have also computed the electron affinity for fluorine, chlorine, bromine, and iodine ions and they are 2.80, 3.84, 3.78, and 3.62 eV as compared to the experimental values[28] 3.4, 3.61, 3.36, and 3.06 eV and the corresponding HF values[29] 1.36, 2.58, 2.58, and 2.54 eV. Of course, one can obtain more reliable values but at the cost of much more work (see, for example, a recent study on electron affinity of bromine in Ref. 30). Finally, to complete our investigation with the present prescription of a soft Coulomb hole model we have verified that there is no appreciable change in the computed $E_c$ with a different choice of basis set. In Table II we present the $E_c$ estimates for neon and zinc with a number of different basis functions. The variations in $E_c$ estimates are not appreciable enough to cause alarm.

In conclusion it appears that the present model offers an avenue to provide a reasonable estimate of the $E_c$ for atoms. It has been argued[17] that perhaps it is too optimistic today to think of available *ab initio* techniques as being practical and fully satisfactory for quantum-mechanical computations of large molecules including electron correlation. Since this situation is changing very slowly despite the remarkable progress of computer technology and software, the present empirical model may be of some utility.

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