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# Linear coupled-cluster method. II. Analysis of local exchange-correlation potentials in beryllium and its isoelectronic series

S. Shankar and P. T. Narasimhan
*Department of Chemistry, Indian Institute of Technology, Kanpur 208016, Uttar Pradesh, India*

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The Slater $X\alpha$ method and its local-potential modifications are examined with reference to the many-electron exchange-correlation effects in the beryllium atom and its isoelectronic series. The linear coupled-cluster method and a hierarchy of approximations to it are employed for this purpose. The role of the exchange parameter $\alpha$ in providing an accurate description of the exchange-correlation effects is analyzed in the light of the electron-gas model. It is found that for Be atoms an $\alpha$ value of 0.768, that which causes the local potential to mimic the Hartree-Fock potential, is the best suited reference state for many-body calculations. The impact of the $\alpha$ variation on the exchange-correlation corrections in the Be isoelectronic series is assessed. With increase in the nuclear charge $Z$, exchange-correlation corrections favor the use of $\alpha$ values closer to $\frac{2}{3}$, the Gaspar-Kohn-Sham limit, in the $X\alpha$ model. The instabilities in the cluster equations induced by ring-diagram terms are also noted. The futility of using gradient corrections to the $X\alpha$ model to account for exchange-correlation effects is brought out in the calculations. It is found that a simple scaling of the electron-gas potential results in excellent single-particle reference states for many-body calculations.

## I. INTRODUCTION

The Slater $X\alpha$ method[1] is a local-density reformulation of the Hartree-Fock self-consistent method. The basic tenet of the $X\alpha$ method is the approximation of the electron density distribution in atoms by the uniform charge density of the electron gas. The one-electron equations of the $X\alpha$ method,

$$\left[\frac{-\hbar^2}{2m}\nabla^2+V(r)+\int\frac{\rho(r)}{|r-r'|}dr' - 3\alpha\left[\frac{3}{4\pi}\rho(r)\right]^{1/3}\right]\Phi_i(r)=e_i\Phi_i(r) \qquad (1)$$

contain the kinetic, nucleus-electron attraction, the electronic Coulomb repulsion, and the exchange energy terms; the last-mentioned term represents the uniform electron-gas approximation to exchange energy. The adjustable empirical parameter $\alpha$ is introduced to take into account a part of the nonuniformity of the electron distribution in atoms.[2] The original derivation of Slater[3] resulted in a value of $\alpha=1$, while the variational derivation of Gaspar[4] and Kohn and Sham[5] yielded a value of $\frac{2}{3}$ for $\alpha$. The last term in the left-hand side of Eq. (1) is strictly an exchange-correlation term, since it is not exactly equal to the Hartree-Fock exchange term.

The validity of the uniform electron-gas approximation in atomic-structure calculations has been examined by Brueckner.[6] In atoms, regions which are neither too near the nucleus nor far removed can be described as possessing a slowly varying charge distribution and the uniform electron-gas approximation would have reasonable validity. In regions very close to the nucleus the electron density is high, but the density gradient is large and the changes are rapid. In this region of large negative potential energy, the uniform electron-gas approximation leads to spurious densities, thus causing unphysical behavior of the distribution.[7] Nevertheless, this is not a serious shortcoming, for the kinetic energy term dominates the interelectron interaction term close to the nucleus and if the kinetic energy is treated exactly, as is done in the $X\alpha$ method, the use of the uniform electron-gas approximation is reasonable. However, in regions far away from the nucleus the electron density is low and the interelectron term becomes significant in comparison to the kinetic energy term, here the uniform electron-gas approximation breaks down. Also, the uniform electron-gas approximation fails to portray correctly the effects of the long range of the Coulomb interaction owing to its inability to account for the shielding interactions between the electrons.[8]

Several corrections to the electron-gas approximation have been made in order to take into account the nonuniformity of the charge distribution in atoms.[9] The $X\alpha$ method itself is an outcome of this. Use of any $\alpha$ value other than $\frac{2}{3}$ in the $X\alpha$ potential takes it outside the electron-gas-exchange approximation.[10] Values of $\alpha$ higher than the Gaspar-Kohn-Sham (GKS) limit of $\frac{2}{3}$ characterize some nonuniformity of the charge distribution. For systems with higher nuclear charge $Z$, better descriptions are obtained with $\alpha$ values nearer to $\frac{2}{3}$. As $Z$ increases, the high-density region in the atom expands and the uniform charge approximation finds greater justification.[11] Although values of $\alpha$ higher than $\frac{2}{3}$ may account for nonuniformity of charge distribution, there are no rigorous theoretical grounds for choosing $\alpha$. Due to the absence of a variational bound on $\alpha$, the energy decreases with increasing $\alpha$.

An interesting variant of the $X\alpha$ formalism has been proposed by Perdew and Zunger.[12] This self-interaction-corrected local spin-density functional formulation produces more accurate electron densities and improved values for total energy and exchange and correlation contributions. This method also affords a better scheme for obtaining virtual orbitals than does the use of the latter potential. To provide an accurate description of the atomic electron distribution, it is necessary to study the change in the exchange-correlation potential with $\alpha$ variation *vis-à-vis* the many-electron exchange-correlation effects.

Many-body perturbation theory has been employed to study the nonuniform charge distribution in atoms starting with a high-density electron-gas approximation.[13] Ma and Brueckner[14] have treated the nonuniform charge density as a perturbation to high-density electron gas. Their analysis was based on the treatment of the electron-electron interaction to all orders in the ring diagrams and the external field producing the nonuniform density to second order. The ring diagrams yield terms which take into account the Coulombic screening and are extremely important for description of atomic charge distributions. The slow density variation was accounted for by expansion of the exchange-correlation potential in powers of the density gradient. For atomic systems, where regions near the nuclei with high-density gradients exist, the expansion leads to infinite energies. The gradient-corrected exchange-correlation potential has, however, been found to disobey the sum rule.[15] An interesting result of Brueckner's study[6] is the observation that ring diagrams are important for the perturbation series. Other studies,[16,17] using coupled-cluster (CC) methods, also emphasize the role played by these diagrams in electron-gas correlation corrections. In contrast, Sinanoglu's atomic many-electron work,[18] starting with Hartree-Fock reference states, finds ladder diagrams to be more important.

In paper I of this series,[19] we outlined the linear CC methodology and the hierarchy of approximations to it for the calculation of exchange-correlation effects in atoms starting with $X\alpha$ reference functions, and analyzed the pairwise contribution to the exchange-correlation energies in the beryllium atom. This paper describes the application of the linear CC many-body theory[20] and a hierarchy of approximations,[19] to study the exchange-correlation corrections in beryllium and its isoelectronic series and to assess the role played by $\alpha$ in treating the exchange-correlation effects. This paper also examines the use of gradient corrections in the $X\alpha$ model and the relative importance of ring and ladder diagram terms for exchange-correlation corrections.

## II. THEORY

The linear CC method and its hierarchy of approximations, (i) to (vi) described in part I[19] are employed in this paper for the calculation of exchange-correlation corrections in beryllium and its isoelectronic series. The structure of the cluster equations, Eqs. (13) and (14) of paper I, which determine the $t_{\alpha\beta}^{rs}$ coefficients for the exchange-correlation correction calculation, becomes clear if they are rewritten in the following manner:

$$\langle \alpha|\hat{f}|r\rangle + (\langle \alpha|\hat{f}|\alpha\rangle - \langle r|\hat{f}|r\rangle) t_{\alpha}^{r} + A t_{\alpha}^{r} + K_1 = 0 \tag{2}$$

and

$$\langle \alpha\beta|\hat{v}|rs\rangle + (\langle \alpha|\hat{f}|\alpha\rangle + \langle \beta|\hat{f}|\beta\rangle - \langle r|\hat{f}|r\rangle - \langle s|\hat{f}|s\rangle) t_{\alpha\beta}^{rs} + B t_{\alpha\beta}^{rs} + K_2 = 0 \; . \tag{3}$$

$A$ and $B$ are the coefficients of the diagonal terms $t_{\alpha}^{r}$ and $t_{\alpha\beta}^{rs}$, respectively, and $K_1$ and $K_2$ represent the nondiagonal terms with their coefficients. $A$, $B$, $K_1$, and $K_2$ contain the ladder, ring, and other diagram terms, which represent the hole-state scattering interactions occurring via the creation of particle-hole pairs and interactions arising from the scattering between hole-hole, hole-particle, and particle-particle states. In the work of Singhal and Das,[16] the nondiagonal term in Eqs. (2) and (3) was replaced by a constant times the diagonal coefficient and the resulting equations were solved. In our calculations, the diagonal and nondiagonal terms are treated exactly. Approximation (i) considers all the diagram contributions to Eqs. (2) and (3), while approximation (ii) considers only the Eq. (3) containing the $t_{\alpha\beta}^{rs}$ terms; approximations (iii), (iv), and (v) neglect all the ring-diagram terms and consider various ladder-diagram term summations; (vi) gives the second-order Rayleigh-Schrödinger-perturbation-theory (RSPT) approximation. The relative importance of the various diagram contributions can be gleaned from a comparison of the results obtained in the various approximations (i) to (vi).

## III. COMPUTATIONAL ASPECTS

The radial part of Eq. (1) is set up and orbitals and energies are obtained.[21] The Latter modification[22] has been used in generating the orbitals. The radial equations are

$$\left[ \frac{-d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) \right] P_{nl}(r) = E_{nl} P_{nl}(r) \; , \tag{4}$$

$$P_{nl}(r) = r R_{nl}(r) \; , \tag{5}$$

where

$$V(r) = \frac{-2Z}{r} + \frac{2}{r} \int_0^r \Sigma_{n,l} [P_{nl}(t)]^2 dt + 2 \int_r^\infty \Sigma_{n,l} \frac{[P_{nl}(t)]^2}{t} dt + V_{X\alpha} \text{ for } r < r_0 \; ,$$

and

$$V(r) = \frac{-2(Z-N+1)}{r} \text{ for } r > r_0 \; . \tag{6}$$

$V_{X\alpha}$, the Slater exchange potential, is given by

$$V_{X\alpha} = 3\alpha \left[ \frac{3}{4\pi r^2} \Sigma_{n,l} [P_{nl}(r)]^2 \right]^{1/3} \; . \tag{7}$$

The virtual basis set consisting of one $s$-type and six $p$-type $X\alpha$ orbitals are generated and used in the CC calculations. A modified Zare routine[23] has been developed to calculate the Fock-type matrix elements and the $r_{ij}^{-1}$ in-

TABLE I. Results of linear coupled-cluster calculation: $\alpha$ variation and exchange-correlation corrections (in units of $10^{-5}$ hartree). Values in parentheses are total energy (in units of hartree).

| | Approximation | | | | | |
|---|---|---|---|---|---|---|
| $\alpha$ | (i) | (ii) | (iii) | (iv) | (v) | (vi) |
| 0.68 | a | a | −22 404.045<br>(−14.782 995) | −25 129.4250<br>(−14.810 249) | −1897.7925<br>(−14.577 933) | −4310.7810<br>(−14.602 063) |
| 0.72 | −28 863.8570<br>(−14.851 329) | −17 084.9550<br>(−14.733 540) | −19302.3650<br>(−14.755 714) | −17 860.7830<br>(−14.741 298) | −1923.7571<br>(−14.581 928) | −4369.6467<br>(−14.606 387) |
| 0.768 | −9746.7623<br>(−14.663 598) | −10 240.2450<br>(−14.668 532) | −13.778.7920<br>(−14.703 918) | −13 198.0470<br>(−14.698 110) | −1958.4480<br>(−14.585 715) | −4450.4306<br>(−14.610 634) |
| 0.80 | −6859.2434<br>(−14.636 302) | −8107.4418<br>(−14.648 785) | −11 461.7600<br>(−14.682 328) | −11 204.0440<br>(−14.679 750) | −1983.7816<br>(−14.587 548) | −4510.7829<br>(−14.612 818) |
| 0.84 | −5092.8685<br>(−14.619 779) | −6445.2239<br>(−14.633 302) | −9437.6154<br>(−14.663 226) | −9386.6006<br>(−14.662 716) | −2018.1891<br>(−14.589 032) | −4594.3078<br>(−14.614 793) |
| 0.88 | −4241.4928<br>(−14.611 465) | −5354.7283<br>(−14.622 597) | −7968.3180<br>(−14.640 733) | −8061.2239<br>(−14.649 662) | −2055.0989<br>(−14.589 601) | −4685.8230<br>(−14.615 908) |
| 0.92 | −4457.9586<br>(−14.612 840) | −4569.6320<br>(−14.613 956) | −6857.5275<br>(−14.636 835) | −7042.9386<br>(−14.638 689) | −2094.9697<br>(−14.589 210) | −4786.5156<br>(−14.616 125) |
| 1.00 | −1241.1588<br>(−14.575 937) | −3462.1602<br>(−14.593 147) | −5378.2290<br>(−14.617 307) | −5605.6193<br>(−14.619 581) | −2182.4171<br>(−14.585 349) | −5013.4015<br>(−14.613 659) |

[a] Indicates the instability of the cluster equations.

tegrals over the $X\alpha$ orbitals. The linear CC equations in the approximations (i) to (vi) are set up and solved using the LU decomposition algorithm.[24]

## IV. RESULTS AND DISCUSSION

### A. Role of the exchange parameter $\alpha$

The exchange-correlation corrections obtained using the linear CC method and the total energies for the respective $\alpha$ values are presented in Table I. With increasing $\alpha$, the exchange-correlation corrections are generally seen to decrease in all the approximations except in (v) and (vi). The exchange-correlation corrected total energy tends to decrease in magnitude with increase in $\alpha$. The work of Herman *et al.*[25] indicates that inhomogeneity causes the local one-electron potential to increase in magnitude and hence drive the $\alpha$ value above the GKS limit of $\frac{2}{3}$. For higher values of $\alpha$, the exchange-correlation potential can be written as

$$V_{X\alpha} = -3\left(\tfrac{2}{3}+x\right)\left[-\frac{3}{4\pi}\rho(r)\right]^{1/3} . \tag{8}$$

As $\alpha$ increases, the exchange-correlation potential becomes more negative and the repulsive interactions between electrons are decreased, i.e., the electrons tend to get correlated. This is reflected by the decrease in exchange-correlation corrections with increase in $\alpha$. Approximations (v) and (vi) which contain only the particle-particle ladder-diagram term and the second-order RSPT term, display incorrect trends reflecting the shortcomings of partial diagram summations. The results obtained with the exclusion of ring-diagram terms in approximations (iii) and (iv) overestimate the exchange-correlation corrections arising from improper screening of charge at large distances. An interesting feature that merges from our calculations is the ill-conditioning of the equations for cases where $\alpha$ approaches the GKS limit. The origin of this erratic behavior rests with the most divergent terms arising from the ring diagrams; exclusion of the ring diagrams stabilizes the equations as seen in approximations (iii) to (vi) (*vide* Table I entry for $\alpha = 0.68$). From the comparison of the exchange-correlation corrected total energies with non-relativistic experimental energies, it appears that the best value of the former is obtained for a reference state with $\alpha = 0.768$; this $X\alpha$ reference state mimics best the Hartree-Fock counterpart.[26]

TABLE II. Exchange-correlation corrections in $B^+$ using the linear coupled-cluster method. All energies in units of $10^{-5}$ hartree.

| | Approximation | | | |
|---|---|---|---|---|
| $\alpha$ | (iii) | (iv) | (v) | (iv) |
| 0.6667 | −7695.3764 | −7482.7350 | −3041.1873 | −6835.8627 |
| 0.7200 | −7051.5219 | −6945.0998 | −3072.5524 | −6936.6784 |
| 0.7600 | −6635.2321 | −6585.3787 | −3098.3189 | −7019.2298 |
| 0.8200 | −6099.1759 | −6106.9325 | −3140.4789 | −7153.4568 |
| 1.0000 | −4967.7677 | −5037.5205 | −3290.0548 | −7621.9410 |

TABLE III. Exchange-correlation corrections in $C^{2+}$ using the linear coupled-cluster method. All energies in units of $10^{-5}$ hartree.

| $\alpha$ | Approximation<br>(iii) | (iv) | (v) | (vi) |
|---|---|---|---|---|
| 0.6667 | −6943.5014 | −6850.3057 | −3890.5391 | −8597.6926 |
| 0.7200 | −6620.3550 | −6569.6645 | −3923.2230 | −8721.1798 |
| 0.7600 | −6400.9709 | −6374.8716 | −3949.8733 | −8820.6700 |
| 0.8200 | −6105.4934 | −6106.8170 | −3993.4032 | −8980.8207 |
| 1.0000 | −5428.5215 | −5467.8338 | −4144.4496 | −9515.1630 |

TABLE IV. Exchange-correlation corrections in $N^{3+}$ using the linear coupled-cluster method. All energies in units of $10^{-5}$ hartree.

| $\alpha$ | Approximation<br>(iii) | (iv) | (v) | (vi) |
|---|---|---|---|---|
| 0.6667 | −7133.6626 | −7068.7165 | −4662.1036 | −10 179.7050 |
| 0.7200 | −6905.2496 | −6867.4398 | −4698.2472 | −10 327.7660 |
| 0.7600 | −6747.8262 | −6726.3593 | −4727.3879 | −10 445.7030 |
| 0.8200 | −6532.9445 | −6530.4300 | −4774.4806 | −10 633.3450 |
| 1.0000 | −6030.6421 | −6057.6573 | −4935.8323 | −11 250.1030 |

### B. $\alpha$ variation and isoelectronic series

Tables II, III, and IV present the exchange-correlation corrections obtained for $B^+$, $C^{2+}$, and $N^{3+}$ using the linear CC method under approximations (iii) to (vi). For higher $Z$, lower $\alpha$ values are favored for larger exchange-correlation corrections in approximations (iii) to (vi). Increase in $Z$ causes the contraction of the orbitals and homogenizes the charge-density distribution to some extent, thus favoring $\alpha$ values closer to the GKS limit. Whereas for Be, the cluster equations are found to be stable for $\alpha$ values above 0.70 in approximations (i) and (ii), for higher $Z$ they are stable only at increasingly higher values of $\alpha$. The divergence of the ring-diagram summations in the electron-gas model using perturbation theory manifests itself here through the ill-conditioned behavior of the cluster coefficients in approximations (i) and (ii). The exclusion of the ring diagrams as in approximations (iii) to (vi) ensures the good behavior of the equations for all $\alpha$ values.

### C. Gradient corrections to exchange

The gradient corrections to exchange within the $X\alpha$ method[25] have also been examined in the light of exchange-correlation corrections obtained in the linear CC calculations. The exchange potential with gradient corrections is of the form[27]

$$V_{X\alpha}(r)=[\alpha+\beta G(\rho)]V_{X1}(\rho)\ , \tag{9}$$

where

$$G(\rho)=\frac{1}{\rho^{2/3}}\left[\frac{4}{3}\left[\frac{\vec{\nabla}\rho}{\rho}\right]^2-2\frac{\nabla^2\rho}{\rho}\right]\ , \tag{10}$$

$V_{X1}$ is the $X\alpha$ potential for $\alpha=1$, and $\beta$ is an adjustable parameter. The exchange-correlation corrections in the approximations (i) to (vi) have been obtained for the gradient-corrected $X\alpha$ potential in the beryllium atom for three different values of $\beta$ at $\alpha=0.667$ and 0.768. The results are given in Tables V and VI. The gradient corrections are seen to stabilize the cluster equations for $\alpha=0.667$, although poor estimates for exchange-correlation correction are obtained as compared to the gradient-uncorrected case (*vide* Table I). Use of higher $\alpha$ values appear to partially account for the atomic density gradients. The divergence caused by the presence of the $(\nabla^2\rho)\rho^{-4/3}$ term in the gradient expansion (varies as $1/r$ as $r\rightarrow 0$) has been overcome by the introduction of a convergence factor,[27] so that the product of the convergence factor and $G(\rho)$ remains equal to $G(\rho)$ for much larger range of $r$. With the introduction of the convergence factor the exchange-correlation potential has the form

$$V_{X\alpha}=\alpha\left[1+\tanh\left[\frac{\beta}{\alpha}G(\rho)\right]\right]V_{X1}\ . \tag{11}$$

TABLE V. Gradient-correction and exchange-correlation corrections in Be using the linear coupled-cluster method $\alpha=0.667$. Energies in units of $10^{-5}$ hartree. Values in parentheses are total energy (in units of hartree).

| $\beta$ | (i) | (ii) | Approximation<br>(iii) | (iv) | (v) | (vi) |
|---|---|---|---|---|---|---|
| 0.0016 | −3278.4954<br>(−14.592 580) | −4125.9437<br>(−14.601 054) | −13378.3820<br>(−14.693 579 0) | −14213.6810<br>(−14.701 932 0) | −1839.1958<br>(−14.578 187) | −4085.1655<br>(−14.600 647) |
| 0.0023 | −657.7841<br>(−14.566 538) | −2632.6784<br>(−14.586 287) | −11028.1810<br>(−14.670 242 0) | −11134.7520<br>(−14.671 308 0) | −1824.6300<br>(−14.578 206) | −4020.9400<br>(−14.600 169) |
| 0.0030 | −505.0548<br>(−14.565 001) | −1834.8544<br>(−14.578 299) | −9413.5238<br>(−14.655 085 0) | −9258.8639<br>(−14.652 539 0) | −1815.9446<br>(−14.578 109) | −3975.2725<br>(−14.599 703) |

TABLE VI. Gradient-correction and exchange-correlation corrections in Be using the linear coupled-cluster method $\alpha=0.768$. Energies in units of $10^{-5}$ hartree. Values in parentheses are total energy (in units of hartree).

| | | | Approximation | | | |
|---|---|---|---|---|---|---|
| $\beta$ | (i) | (ii) | (iii) | (iv) | (v) | (vi) |
| 0.0016 | −828.7893<br>(−14.574 513) | −2563.8942<br>(−14.591 864) | −8987.0716<br>(−14.656 096) | −8869.2180<br>(−14.654 917) | −1912.6811<br>(−14.585 352) | −4238.7990<br>(−14.608 613) |
| 0.0023 | −410.3095<br>(−14.569 403) | −1670.2231<br>(−14.582 002) | −7925.6058<br>(−14.644 556) | −7728.8740<br>(−14.642 589) | −1899.3797<br>(−14.584 294) | −4171.5107<br>(−14.607 015) |
| 0.0030 | −59.9383<br>(−14.564 564) | −1117.3397<br>(−14.575 138) | −7130.1377<br>(−14.635 266) | −6902.5808<br>(−14.632 991) | −1891.8719<br>(−14.582 884) | −4123.5034<br>(−14.605 200) |

As pointed out by Herman,[25] lower $\beta$ values are seen to be favored for the beryllium atom. The gradient corrections to the $X\alpha$ model are seen not to produce any significant improvements in total energy.

## V. CONCLUSIONS

The import of the study reported in this paper rests on the analysis of the local potential $X\alpha$ approximation. Owing to the use of uniform charge approximation, the $X\alpha$ model shares the problems inherent to electron-gas theories. The ill-behaved terms arising from the ring diagrams indicate the inappropriateness of the unmodified electron-gas approximation for atomic structure studies. However, with a proper scaling of the local potential all the divergences inherent in the electron-gas approximation are seen to be eliminated. Gradient corrections to the $X\alpha$ potential do not cause any significant improvements in the exchange-correlation corrections and total energies. Unlike in Brueckner's study,[6] where only ring diagrams were found to be important, or in Sinanoglu's study,[18] where only ladder diagrams were found to be important, in this study with the $X\alpha$ model, it is found necessary to take into account both ladder- and ring-diagram terms.

It is seen that by using the linear CC method extremely accurate total energies are obtained with proper scaling of the exchange parameter in the reference state. For Be the best scaled value of $\alpha$ is found to be 0.768, a value that causes the reference state to mimic exactly its Hartree-Fock counterpart. However, as $Z$ increases lower $\alpha$ values are preferred and in the limit of very large $Z$ it is inferred that the more homogeneous high-density distribution enables the parent electron-gas model to serve as a good reference state. The accuracy achieved in the many-body calculations with properly scaled reference functions along with the computational simplicity of the linear CC model recommends the use of $X\alpha$ model in such calculations. Further work on nonlinear CC models and the examination of self-exchange corrected $X\alpha$ model is in progress.

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