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CONSTRUCTION OF AN OPTIMIZED Z-INDEPENDENT STATISTICAL EXCHANGE POTENTIAL FOR ATOMIC, MOLECULAR, AND SOLID STATE CALCULATIONS

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Abstract. — The optimized $X_\alpha$ method has the drawback that the optimum value of $\alpha$ for isolated atoms is $Z$-dependent, a consequence of the fact that $V_{X_\alpha}$ has to represent inhomogeneous as well as homogeneous exchange effects. In treating polyatomic molecules and crystals by the $X_\alpha$ method, one is obliged to use spatially discontinuous exchange potentials (muffin-tin approximation or arbitrarily smoothed versions of these). A simple way of avoiding such difficulties is to adopt the $X_{\alpha\beta}$ method, which treats homogeneous and inhomogeneous exchange effects separately, and attempt to find optimum $Z$-independent values for the two parameters $\alpha$ and $\beta$. In this paper, such a universal (Z-independent) $X_{\alpha\beta}$ exchange potential is constructed, and it is shown that except for the very lightest atoms (He and Li), the choice $\alpha = 2/3$ and $\beta = 0.003$ leads to an exchange model which is superior to the optimized $X_\alpha$ model, at least on the basis of the Hartree-Fock total energy criterion. The choice $\alpha = 2/3$, suggested by theoretical considerations, is supported by empirical studies. The choice $\beta = 0.003$ is not particularly critical. The universal optimized $X_{\alpha\beta}$ exchange potential described here should prove particularly useful in applications to polyatomic molecules and crystals, including self-consistent electronic structure calculations.

I. Introduction. — The presence of the non-local exchange operator in the Hartree-Fock equations for a many-electron system greatly complicates the numerical solution of these equations. In 1951, Slater [1] called attention to the practical advantages of the statistical exchange approximation and advocated the use of the local exchange potential

$$V_{XS} = -6[(3/8 \pi) \rho(r)]^{1/3} \text{Ryd}$$

in place of the non-local HF exchange potential. Subsequently, Gaspar [2] and Kohn and Sham [3] proposed the use of an alternate approximate exchange potential which differs from $V_{XS}$ by a factor of $2/3$:

$$V_{X\text{GKS}} = (2/3) V_{XS}.$$ 

During the past several years, both of these exchange approximations have been widely used in atomic and solid state calculations. Examples of the latter include studies of Ni by Connolly [4], of Cu by Snow and Wafer [5], and of Li by Rudge [6]. The results of such studies are usually in reasonable agreement with experiment; in fact, the theoretical results based on $V_{XS}$ and $V_{X\text{GKS}}$ often bracket the corresponding experimental results.

This state of affairs led to the development of the so-called $X_\alpha$ method [7], according to which the exchange potential is represented by $V_{X_\alpha} = \alpha V_{XS}$, where $\alpha$ is a suitably chosen parameter lying between $2/3(V_{X\text{GKS}})$ and $1(V_{XS})$. In some studies, $\alpha$ is chosen empirically with a view to bringing the overall theoretical results into the closest possible agreement with experiment. Values of $\alpha$ determined in this manner would in general be expected to be different for different electronic systems.

In other studies, the choice of $\alpha$ is dictated by theoretical rather than empirical considerations.

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Abstract. — Nous construisons ici un tel potentiel d'échange et essayons de trouver des valeurs optimales, indépendantes de $Z$, pour les deux paramètres $\alpha$ et $\beta$. Nous montrons que, sauf pour les atomes très légers (Li et He), le choix $\alpha = 2/3$ et $\beta = 0.003$ conduit à un modèle qui est meilleur que celui de la méthode $X_\alpha$ optimisée, du moins en se basant sur le critère de l'énergie totale Hartree-Fock. Le choix $\alpha = 2/3$, suggéré par des considérations théoriques, se justifie empiriquement. Le choix $\beta = 0.003$ n'est pas très critique. Le potentiel d'échange universel $X_{\alpha\beta}$ présenté ici devrait se montrer particulièrement utile dans les applications aux molécules polyatomiques et les cristaux.
Unfortunately, the choice of \( \alpha \) on theoretical grounds (see next section) leads to values of \( \alpha \) which differ from atom to atom. Thus, if one is attempting to construct an approximate exchange potential for a polyatomic molecule or a crystal containing more than one atomic species in the unit cell, one is forced to use different values of \( \alpha \) in different regions of space. This difficulty is obscured but not eliminated when the calculations are based on the muffin-tin approximation. In fact, with a muffin-tin potential, one may have to use different values of \( \alpha \) in different types of atomic spheres, and still a further value of \( \alpha \) in the flat portion of the muffin-tin. Thus, an approach which starts out with the objective of determining \( \alpha \) on theoretical grounds soon assumes a semi-empirical character, in that the choice of atomic sphere radii and of \( \alpha \) in the flat portion are arbitrary within certain limits. Clearly, one can choose atomic sphere radii and the interstitial \( \alpha \) so as to bring theory and experiment into closest possible agreement, even if the values of \( \alpha \) within the spheres are chosen on theoretical grounds. A further difficulty is: how does one perform unique and unequivocal self-consistent calculations under these circumstances?

In view of the growing importance of statistical exchange calculations in atomic, molecular, and crystalline systems, it is essential to overcome the difficulties associated with a \( Z \)-dependent \( \alpha \). It has already been demonstrated in two earlier papers by Herman and co-workers [8], [9] that the inclusion of the second-order exchange inhomogeneity correction \( \beta G(\rho) V_{\text{XS}} \) leads to an improved exchange potential of the form

\[
V_{\text{Xa}} = \left[ \alpha + \beta G(\rho) \right] V_{\text{XS}};
\]

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

where \( \alpha \) and \( \beta \) can both be regarded as arbitrary parameters. However, detailed studies on a number of representative atomic systems [8], [9], [10] indicate that \( V_{\text{Xa}} \) with \( \alpha \) fixed at 2/3 and \( \beta \) varying only slightly from atom to atom is superior to \( V_{\text{Xa}} \) in the sense that the Hartree-Fock expression for the total energy yields values significantly and systematically closer to the exact Hartree-Fock values when this expression is evaluated using \( Xa\beta \) rather than \( Xa \) atomic orbitals. Although some writers have argued that the \( Xa \) method is to be preferred to the \( Xa\beta \) method because the former is computationally simpler than the latter, actual experience with both methods clearly indicates that inclusion of the inhomogeneity terms in the latter is quite simple, and that the effort involved in taking these terms into account is negligible compared to setting up the \( Xa \) method in the first place. In our judgment, the advantages inherent in the \( Xa\beta \) method easily offset the slight amount of extra effort involved in setting this method up.

II. Choice of \( \alpha \) in the \( Xa \) method: theoretical considerations. — Before turning to the optimum choice of \( \alpha \) and \( \beta \) in the \( Xa\beta \) method, it is desirable to review three procedures that have already been used in determining optimum values of \( \alpha \) in the \( Xa \) method:

a) In the first of these procedures, the objective is to find a set of atomic orbitals which when substituted into the Hartree-Fock expression for the total energy yields a result which is as close to the exact Hartree-Fock energy as possible. According to this approach, which was suggested by Lindgren [11], one finds a series of self-consistent atomic solutions corresponding to different choices of \( \alpha \), and then one adopts as the optimum value of \( \alpha \) that which leads to a minimum value of the Hartree-Fock total energy \( E_{\text{HF}} \) (cf. Fig. 1).

![Fig. 1.](image)

This so-called minimum \( E_{\text{HF}}^\alpha \) criterion leads to an optimum value of \( \alpha \) which we will denote by the symbol \( \alpha_{\text{min}} \). Knetko [12] and Wood [13] have obtained values of \( \alpha_{\text{min}} \) for a number of atoms (cf. Fig. 2). Their results clearly indicate the \( Z \)-dependence of \( \alpha_{\text{min}} \).

b) A second procedure for choosing an optimum value of \( \alpha \) was suggested by Berrondo and Gosciniski [14] and independently by McNaughton and Smith [15]. Here, one evaluates the virial coefficient

\[
\eta = - \langle V \rangle / \langle T \rangle
\]

using the Hartree-Fock expressions for \( \langle V \rangle \) and \( \langle T \rangle \) with different sets of \( Xa \) orbitals, and then
one chooses $\alpha (= \alpha_{HF})$ by the requirement that $\eta = 2$, i.e., that the virial theorem be satisfied.

c) A third approach due to Slater and Wood [7] fixes $\alpha (= \alpha_{HF})$ by the condition that the $X\alpha$ orbitals yield a value for the total energy in the statistical approximation $E_{STAT}^\alpha$ that matches the exact (assumed known) Hartree-Fock total energy. The latter quantity is given, for example, by the configuration-averaged Hartree-Fock results of Mann [16]. Schwarz [17] has shown that procedures b) and c) lead to nearly the same optimum values of $\alpha$ for a number of atoms.

While a plot of $\alpha_{min}$ vs $Z$ shows some scatter (cf. Fig. 2), plots of $\alpha_{HF}$ or $\alpha_{min}$ vs $Z$ show a linear variation in each range of $Z$ where a given shell is being filled. Lindgren and Schwarz [18] have discussed this segmented linear variation. On the basis of references [8] and [9], it can be argued that the $Z$ variation of $\alpha$ arises because the homogeneous exchange term is required, in the $X\alpha$ method, to account for inhomogeneous as well as homogeneous exchange effects, and the former are different for different shells. In the $X\alpha\beta$ method, homogeneous and inhomogeneous exchange effects are represented by separate terms, so that each of these has a better chance of being represented by a $Z$-independent quantity.

In references [8] to [10] the minimum Hartree-Fock total energy criterion (a) was used to determine values of $\alpha$ and $\beta$, and it was found that the minimum total energy found in this manner was consistently lower than that given by the same criterion according to the $X\alpha$ method. Thus, the optimum value of $E_{HF}^{\alpha\beta}$ was consistently closer to the exact Hartree-Fock total energy than the optimum value of $E_{HF}^\alpha$.

### III. X$\alpha\beta$ method: improved treatment of convergence factors.

There is one practical difficulty with the $X\alpha\beta$ method that deserves comment, namely, that the function $G(\rho)$ becomes singular at very large and very small values of $\rho$. This feature of $G(\rho)$, already discussed in reference [8] and in the appendix of reference [9], does not affect the calculation of the total energy since all the energy integrals converge, but does prove a nuisance from the standpoint of solving the radial wave equation using the Herman-Skillman atomic structure program [19]. In references [8] and [9] the singularities were removed by the use of small-$r$ and large-$r$ convergence factors. In this paper we will adopt a modified treatment of the convergence factors which is more convenient than that used earlier. We will henceforth represent the exchange potential by the form

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

In the range of $r$ where $G(\rho)$ is well-behaved, the absolute value of the argument of $\tanh$ is smaller than 0.25, so that $\tanh x$ deviates from $x$ by less than 2%. At large and small $r$, where $G(\rho)$ diverges, the modulation function

$$M(\rho) = \tanh \left(\frac{\rho}{\alpha} G(\rho)\right)$$

reaches the limits ± 1. The modulation function $M(\rho)$ is shown for atomic Ti in figure 3 with $\alpha = 2/3$ and

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**Fig. 2.** $Z$ dependence of the exchange parameter $\alpha$ in the $X\alpha$ scheme calculated in two different ways. The solid dots denote values of $\alpha_{HF}$ as determined by Schwarz [17] by matching the statistical total energy to the HF value. The triangles and squares denote values of $\alpha_{min}$ as obtained by Kmetko [12] and Wood [13] by minimizing the expectation value of the HF total energy using $X\alpha$ orbitals (after Schwarz [17]).

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**Fig. 3.** The modulation function $M(\rho)$ displayed on a logarithmic radial scale for titanium. The radial spherical charge density $\sigma$ is also shown for reference.
\( \beta = 0.003 \). The radial charge density \( \sigma = 4 \pi r^2 \rho \) is also shown for purposes of comparison. It will be noted that the minima of \( M(\rho) \) and \( \sigma(\rho) \) occur at the same radial distances.

IV. Numerical results. — Using the modified \( X\alpha\beta \) method just described, the exchange parameter \( \beta \) was optimized for the atoms He through Ar plus some additional ones (with \( \alpha \) fixed at 2/3). The Latter tail correction [20] was not used here or elsewhere in this paper. In these runs, two optimization procedures were used: \( a) \) minimization of the HF total energy; and \( b) \) satisfaction of virial theorem. Illustrative results for atomic Ti are shown in figures 1 and 4. Clearly, there is a wide range of \( \beta \) for which \( E^\alpha_{HF} \) is lower than the optimum value of \( E^\alpha_{HF} \), namely

\[ 0.000 6 < \beta < 0.005 7. \]

Moreover, the optimum values of \( \beta \) according to these two criteria, \( \beta_{\text{min}} \) and \( \beta_{\text{vt}} \), are reasonably close to one another. This suggests that the choice of the optimum \( \beta \) is not particularly critical, and that one can improve on the \( X\alpha \) method by using any value of \( \beta \) within reasonable limits for a given atom.

The next question is: can one find a universal value of \( \beta_{\text{min}} \) or \( \beta_{\text{vt}} \) which lies within fixed limits for a large number of atoms? In figures 5 and 6 we show the differences between \( E^\alpha_{HF} \) and \( E^\alpha_{HF} \) (exact Hartree-Fock total energy) for a large number of atoms plotted as a function of \( \beta \). In all these cases the value of \( \alpha \) has been set at 2/3. Considering the fine energy scale, all the curves are quite flat in the neighborhood of say \( \beta = 0.003 \).

Moreover, the values of \( \beta_{\text{vt}} \) (virial theorem criterion) are nearly independent of \( Z \) except for the very lightest atoms. This suggests very strongly the possibility of using one set of parameters for all atoms, say \( \alpha = 2/3 \) and \( \beta = 0.003 \). Accordingly, we propose a universal exchange potential \( V_{X\alpha\beta} \) with fixed \( \alpha \) and \( \beta \) parameters:

\[ V_{X\alpha\beta} = [1 + \tanh \{ 3/2 \times 0.003 G(\rho) \}] / \theta \]

where \( F \) indicates that \( \alpha \) and \( \beta \) have been frozen (fixed).

A comparison of the three exchange approximations \( X\alpha, X\alpha\beta \), and \( XPF\beta \) is shown in figure 7 in the form of a
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He LiBeB C N O FNeNaMgAlSi P SCIAr

FIG. 7. — Z dependence of the difference in the expectation value of the HF total energy between one of the statistical approximations and the exact HF value. Solid line shows $E_{\alpha}^\text{HF} - E_{\text{HF}}$ (with $\alpha_{\text{min}}$ in $X\alpha$ scheme), dashed line illustrates $E_{\alpha\beta}^\text{HF} - E_{\text{HF}}$ with $\alpha = 2/3$ and $\beta_{\text{min}}$. The crosses indicate the values $E_{\alpha\beta}^\text{HF} - E_{\text{HF}}$ corresponding to the exchange potential $V_{X\alpha\beta}$.

plot of $E - E_{\text{HF}}$ vs atomic number, where $E = E_{\alpha}^\text{HF}$; $E_{\alpha\beta}^\text{HF}$, $\alpha = 2/3$; and $E_{\text{HF}}$, $\alpha = 2/3$, $\beta = 0.003$. Except for the very lightest atoms, the $X\alpha\beta$ as well as the $X\alpha\beta\beta$ methods with $\alpha = 2/3$ lead to better values of the HF total energy than does the $X\alpha$ method. Moreover, the universal exchange potential $V_{X\alpha\beta\beta}$ with $\alpha$ and $\beta$ fixed leads to HF total energies that are virtually identical to those obtained by holding $\alpha$ fixed at $2/3$ and optimizing $\beta$ via criterion $a)$. In assessing the implications of figure 7, it should be borne in mind that $E_{\text{HF}}$ varies from $-5.7$ Ryd for He to about $-1054$ Ryd for Ar.

Up to this point, the parameter $\alpha$ was set at 2/3 in the $X\alpha\beta$ method (because this is the theoretical value for the homogeneous term according to references [2] and [3]). In figure 7 we saw that at least for He and Li the $X\alpha\beta$ method with $\alpha = 2/3$ led to slightly poorer results than the $X\alpha$ method. In figure 8 we show, for atomic He, the consequences of treating both $\alpha$ and $\beta$ as adjustable parameters in the $X\alpha\beta$ method. For $\beta \geq 0$, the minimum value of $E_{\alpha\beta}^\text{HF}$ corresponds to the case $\beta = 0$. To improve upon the optimized $X\alpha$ method in this case, we would have to use a negative value of $\beta$.

In the case of atomic Ti, it is possible to obtain slightly better values for $E_{\alpha\beta}^\text{HF}$ by varying both $\alpha$ and $\beta$, as can be seen from figure 9, but the improvement over the previous choice, where $\alpha$ is fixed at 2/3 and only $\beta$ is adjustable, is negligible. Thus, for most of atoms that we have studied, we do not expect to gain much by treating both $\alpha$ and $\beta$ as adjustable parameters.

V. Conclusions. — It is possible to construct a universal (Z-independent) statistical exchange potential of the form

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

which leads to total Hartree-Fock energies that are consistently closer to the exact Hartree-Fock total energies than are those given by the $X\alpha$ method, except for the very lightest atoms (He and Li). If one uses this universal exchange potential in studies of molecules and polyatomic solids, one can avoid the use of a spatial and Z-dependent $\alpha$ parameter in the $X\alpha$ method, a most unphysical feature of this method [21], [22], [23].

In the above expression, we recommend the choice

FIG. 8. — $\alpha$ and $\beta$ dependence of $E_{\alpha\beta}^\text{HF} - E_{\text{HF}}$ for He. Dashed line indicates the standard choice of $\alpha$ in the $X\alpha\beta$ method.

FIG. 9. — Same as figure 8 for Ti.
\( \alpha = 2/3 \) and \( \beta = 0.003 \), though any choice of \( \beta \) in the range 0.002 to 0.004 would serve nearly as well. The tanh function has been introduced as a numerical convenience to eliminate the divergences of this potential at very large and very small values of \( r \). Finally, it should be emphasized that in the present study we have not concerned ourselves with correlation effects, but have attempted merely to approximate the non-local Hartree-Fock exchange potential by a physically realistic, computationally tractable, universal (Z-independent) local exchange potential. As the theory of exchange-correlation potentials becomes further developed, it will become increasingly important to find simple approximations for such potentials as well [24].

VI. Acknowledgment. — The authors are pleased to acknowledge helpful discussions with Dr. Irene B. Ortenburger, whose atomic structure programs including exchange inhomogeneity terms were used as the starting point of the present investigation. One of us (KS) wishes to thank the IBM San Jose Research Laboratory for its hospitality during his stay there during the summer of 1971. The authors are grateful to Dr. William E. Rudge and Dr. Norris W. Dalton for constructive criticism of the manuscript.

References

[7] For a review of the \( X \alpha \) method with additional references see for example: Slater (J. C.), Wood (J. H.), Intern. J. Quantum Chem., 1971, 45, 3.

In this paper it is shown that the optimum value of \( \beta_{0} \) for several atoms (Ne, K, Mn, Cu, As, Te, Sb and Eu) is 0.004 ± 0.000 4 (when no latter tail is employed). Although Boring’s results demonstrate the universality (Z-independence) of the \( \beta_{0} \) criterion and in this sense are consistent with our present results, his universal \( \beta_{0} \) is 0.004, which is to be contrasted with our own value of 0.003. In unpublished work, Dr. I. B. Ortenburger has verified that our \( \beta_{0} \) for such atoms as Kr, Xe, and Rn is consistently 0.003. We believe that the difference between Boring’s value of \( \beta_{0} = 0.004 \) and our value \( \beta_{0} = 0.003 \) is due to the use of different convergence factors. While Boring uses the convergence factors that we ourselves introduced in reference [8], our present results are based on the form \( V_{XG} = aV_{X}(1 + \tanh \beta G(x))/G(\rho) \), where-in the convergence factors are automatically taken into account via the hyperbolic tangent function. Whether this is in fact the source of the difference is currently under investigation.