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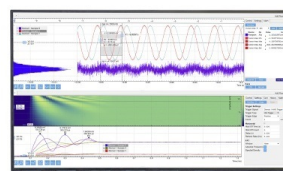The Journal of Chemical Physics **132**, 154104 (2010); https://doi.org/10.1063/1.3382344

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On some approximations in applications of $X\alpha$ theory

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An approximate $X\alpha$ functional is proposed from which the charge density fitting equations follow variationally. LCAO $X\alpha$ calculations on atomic nickel and diatomic hydrogen show the method independent of the fitting (auxiliary) bases to within 0.02 eV. Variational properties associated with both orbital and auxiliary basis set incompleteness are used to approach within 0.2 eV the $X\alpha$ total energy limit for the nitrogen molecule.

I. INTRODUCTION

The multiple scattering method (MS$X\alpha$),[1] as applied to the $X\alpha$[2] theory of many-electron systems, has proven quite successful in predicting one-electron properties of close-packed molecules.[3] However MS$X\alpha$ is unreliable in studies of molecular geometry[4] a failure due principally to the use of a muffin-tin (MT) approximation for the potential.[5] Much work has been directed towards removing this approximation using both MT[6] and analytic (LCAO)[7–9] orbital basis (OB) functions. In contrast with LCAO Hartree–Fock (HF) methods, the number of significantly different LCAO$X\alpha$ methods is large and increasing. Fundamentally this situation stems from the nonanalytic dependence of the $X\alpha$ exchange energy on the electronic charge density necessitating other than direct analytic evaluation of this energy which can introduce errors beyond the incompleteness of the OB. Such methods are not strictly variational, affecting the reliability of calculated total $X\alpha$ energies in particular.

It is the purpose of this paper to address the effects of some of the approximations in various nonmuffin-tin (NMT) $X\alpha$ total energy calculations. We are particularly interested in the effects of fitting which appears to a greater or lesser extent in all current molecular LCAO$X\alpha$ methods. This work was stimulated by the difficulty encountered in applying the Gaussian-type-orbital (GTO) method of Sambe and Felton[8] to larger systems,[10,11] and we hope to stimulate further research towards minimizing the errors in the total molecular $X\alpha$ energy as computed by the various methods. Ultimately these efforts may produce an economical and reliable $X\alpha$ or other[12] similar density functional[13,14] method for computing properties of large molecules.

The organization of this paper is as follows. Section II contains a review of $X\alpha$ theory and a discussion of some of its molecular implementations. In Sec. III we explore in some depth the error made in fitting the charge density and show that the $X\alpha$ functional can be modified such that the calculated $X\alpha$ energy is stationary with respect to changes in the charge density fitting basis (CDB) set. Methods for treating the exchange potential are discussed in Sec. IV. Section V contains the results of various LCAO$X\alpha$ calculations on atomic nickel and diatomic hydrogen and nitrogen. For these light diatomics our binding energies and internuclear separations are near their true $X\alpha$ values.

II. THE $X\alpha$ MODEL AND METHODS

Within the $X\alpha$ model, the total energy (in hartree atomic units) is given by

$$EX\alpha = \sum_i n_i \int \phi_i^*(1)\left[-\tfrac{1}{2}\nabla_1^2 - \sum_p Z_p/r_{1p}\right]\phi_i(1)\,dr_1$$
$$+ U_c + U_x + \frac{1}{2}\sum_{p>q} Z_p Z_q/r_{pq} \,, \qquad (2.1)$$

where n_i is the occupation number of the ith orbital ϕ_i. The self-energy of the electronic charge distribution is

$$U_c = \frac{1}{2}\int \rho(1)\rho(2)/r_{12}\,dr_1 dr_2 \qquad (2.2)$$

where

$$\rho(1) = \sum_i n_i \phi_i^*(1)\phi_i(1) \,. \qquad (2.3)$$

The average exchange energy of a homogeneous electron gas is

$$U_x = C\int \rho(1)^{4/3}\,dr_1 \,, \qquad (2.4)$$

with

$$C = -\alpha\,\tfrac{3}{4}\left(\tfrac{81}{8\pi}\right)^{1/3} \,.$$

The parameter α empirically accounts for the energy dependence of the exchange which falls to $\tfrac{2}{3}$ of the above value at the Fermi energy.[14,15] (While the value of $\tfrac{2}{3}$ is theoretically justified a somewhat larger value is needed to approximate the contributions from atomic core regions where the electronic density is far from homogenous.) Open shell systems can be treated by introducing a spin dependence into the exchange energy, Eq. (2.4).

The one-electron equations follow variationally from

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0021-9606/79/203396-07$01.00

Eq. (2.1),

$$\epsilon_i \phi_i(1) = \left[-\tfrac{1}{2}\nabla_1^2 - \sum_p Z_p/r_{1p} + V_c(1) + V_x(1) \right] \phi_i(1)$$

$$\equiv \hat{h}\phi_i(1) \ , \tag{2.5}$$

where

$$V_c(1) = \int \rho(2)/r_{12}\, d\mathbf{r}_2 \ , \tag{2.6}$$

and

$$V_x(1) = \tfrac{4}{3} C \rho(1)^{1/3} \ . \tag{2.7}$$

These equations can be used to eliminate various terms from Eq. (2.1). For example,

$$E = \sum_i n_i \epsilon_i - U_c - \tfrac{1}{3}U_x \ , \tag{2.8}$$

where the kinetic energy has been eliminated. However, this substitution precludes direct evaluation of the virial ratio or other term by term tests of the accuracy to which the total energy is calculated.

The MSXα method was the first application of Xα to molecules. Its computational details can be found elsewhere.[1] In principle the method can yield an exact solution of the Xα equations for a muffin-tin molecular potential, since the MSXα one-electron equations follow variationally from a MT Hamiltonian.[6] In practice the method is not variational in the number of partial waves[16] due to truncations of internal summations.[17] However, the convergence of the method in partial waves is remarkably rapid, and this effect is insignificant compared to the MT approximation. These problems can be removed via first order perturbation theory[5,6] or via matrix diagonalization in a finite basis set in the manner of Gunnarsson, Harris, and Jones.[12] However, OB incompleteness will leave a residual MT effect. Within the limits of first order perturbation theory, Ringers and Danese[18] found small but not insignificant effects associated with MT size changes. Such effects could fold unphysical forces into calculated total energy surfaces.

LCAOXα methods face several hurdles. One, which on the surface is rather minor, is the analytical intractability of a direct evaluation of the exchange energy Eq. (2.4). The exchange potential Eq. (2.7), being proportional to the cube root of the charge density, is slowly varying and nodeless and as such is quite easy to treat numerically or to fit using a small three dimensional (3D) grid of points.[8] However, the need to approximate at this step opens the door psychologically to further, potentially more consequential approximations. Another hurdle comes in the evaluation of the electronic repulsion energy Eq. (2.2). While this energy can be computed exactly, the temptation not to do so is twofold. First, in LCAO methods this computation involves evaluating a number of integrals that grows as the fourth power of the number OB functions (the same N^4 problem that is the bottleneck for HF methods). Secondly, three and four-center integrals can arise which are quite cumbersome particularly in a Slater-type-orbital (STO) method.

The discrete variational method DVM[7] is the most

commonly used LCAOXα method. In this scheme the STO expansions of the one-electron wave functions,

$$\phi_i(1) = \sum_n c_{in} X_n(1) \ , \tag{2.9}$$

are determined from the usual secular equation,

$$\mathbf{Hc}_i = \epsilon_i \mathbf{Sc}_i \ ,$$

where a 3D grid of sampling points $\mathbf{r}_k$ and weights w_k are used to approximate the necessary matrix elements

$$H_{mn} = \sum_k w_k X_m(\mathbf{r}_k)\, \hat{h}\, X_n(\mathbf{r}_k) \ , \tag{2.10}$$

and

$$S_{mn} = \sum_k w_k X_m(\mathbf{r}_k) X_n(\mathbf{r}_k) \ . \tag{2.11}$$

Typically the number of sampling points is kept below what is necessary for accurate (effective) numerical integration. A frozen core is used to avoid orthogonality problems introduced by approximating the overlap matrix Eq. (2.11).

To circumvent the N^4 problem the charge density is fit,

$$\rho(1) \simeq \tilde{\rho}(1) = \sum_i a_i f_i(1) \ , \tag{2.12}$$

and thus the electronic potential is approximated

$$V_c(1) \simeq \tilde{V}_c(1) = \int \tilde{\rho}(2)/r_{12}\, d\mathbf{r}_2 \ . \tag{2.13}$$

(Following convention,[7] a tilde indicates a fitted quantity.) That this can result in a computational saving is seen by noting that the charge density is nodeless—the OB flexibility necessary to position the nodes of the one-electron wave functions need not be present in the CDB.

Apart from the approximation to the electronic potential Eq. (2.13) the pointwise contributions to the secular matrix elements Eqs. (2.10)–(11) are computed exactly and analytically. As originally proposed,[7] the total energy is computed via Eq. (2.8) with

$$U_c \simeq \tilde{\tilde{U}}_c = \frac{1}{2} \int \tilde{\rho}(1)\tilde{\rho}(2)/r_{12}\, d\mathbf{r}_1\, d\mathbf{r}_2 \ ,$$

(the double tilde indicates a double dependence on fitted quantities) and U_x determined by numerical integration.

This ($\sim N^2$) method is quite economical and yields excellent one-electron properties[19] but is rather unreliable in total energy calculations due to the nonvariationality introduced by fitting and numerical sampling. Recently the accuracy of the method has been increased[20] principally by evaluating all contributions to the total energy analytically except U_x and increasing the number of auxiliary functions in the CDB to the limit of numerical stability.[21]

In a newer LCAOXα variation, Sambe and Felton[8] have proposed fitting the exchange,

$$V_x(1) \simeq \tilde{V}_x(1) = \sum_i b_i g_i(1) \ , \tag{2.14}$$

This introduces an entire set of auxiliary basis func-

tions, the exchange fitting basis (XB), in addition to the CDB. By changing to GTO bases, the secular matrix elements can easily be evaluated analytically,

$$H_{mn} = \int X_m(1)\hat{h}X_n(1)\,dr_1 \tag{2.15}$$

and

$$S_{mn} = \int X_m(1)X_n(1)\,dr_1 \ . \tag{2.16}$$

This method is more expensive computationally ($\sim N^3$) than the DVM due to the need to evaluate the three-center integrals contributing to

$$U_c \simeq \tilde{U}_c = \frac{1}{2}\int \rho(1)\tilde{\rho}(2)/r_{12}\,dr_1\,dr_2$$

and

$$U_x \simeq \tilde{U}_x = C\int \rho(1)\tilde{\rho}(1)^{1/3}\,dr_1$$

On the other hand, more of the calculation is done analytically reducing the size of the sampling grid (now used only in Eq. (2.14)). Applications of the method to small molecules and limited to s type and atom-centered auxiliary functions[8,22] were encouraging. The method has also been used successfully with nonspherical[16] and off-center[11] additions to the auxiliary bases. However for large systems the CDB becomes extremely large[11] and numerically unstable.[10]

The STO-3G (three-Gaussian expansion of a minimal STO OB)[23] $X\alpha$ method of Koller, Zaucer, and Azman treats U_c exactly. The exchange is numerically least squares fit to

$$V_x(1) = \tfrac{4}{3}C\rho(1)^{1/3} \simeq \sum_i b_i \,|\,g_i(2)\,|^2 \ ,$$

where g_i is a three-Gaussian expansion of the cube root of a parent STO OB function. (The directional attributes of the exchange fit enter through the expansion of the cube root of p-type STOs). Since only the exchange is treated approximately, this method is probably very close to being variational although offering little if any computational advantage relative to HF methods. The use of minimal basis sets in these calculations prevents an exact evaluation of the $X\alpha$ total energy.

III. FITTING THE CHARGE DENSITY

In an economical, extended basis set LCAO$X\alpha$ scheme the electronic Coulomb potential must be treated approximately since the direct evaluation of U_c requires $\sim N^4$ integrations. The only approximation in widespread use is fitting which we now examine.

In their DVM method Baerends, Ellis, and Roos[7] found the linear expansion coefficients a_i in Eq. (2.12) by conventional constrained least squares fit methods. That is by minimizing

$$D = \int (\rho(1) - \tilde{\rho}(1))^2\,dr_1 \tag{3.1}$$

subject to the norm preserving constraint,

$$\int \tilde{\rho}(1)\,dr_1 = \sum_i a_i \int f_i(1)\,dr_1 \equiv \mathbf{a} \cdot \mathbf{n} = N_e \ , \tag{3.2}$$

where N_e is the number of electrons. Defining

$$t_i = \int \rho(1)f_i(1)\,dr_1$$

$$S_{ij} = \int f_i(1)f_j(1)\,dr_1 \ , \tag{3.3}$$

D is minimized subject to Eq. (3.2) by

$$\mathbf{a} = \mathbf{S}^{-1}(\mathbf{t} + \lambda\mathbf{n}) \ , \tag{3.4}$$

where the Lagrange multiplier λ is given by

$$\lambda = (N_e - \mathbf{n} \cdot \mathbf{S}^{-1} \cdot \mathbf{t})/\mathbf{n} \cdot \mathbf{S}^{-1} \cdot \mathbf{n} \ . \tag{3.5}$$

To analyze the errors associated with this procedure it is convenient to define

$$\rho = \tilde{\rho} + \Delta\rho \ ,$$

in which case

$$U_c = 2\tilde{U}_c - \tilde{\tilde{U}}_c + \frac{1}{2}\int \Delta\rho(1)\,\Delta\rho(2)/r_{12}\,dr_1\,dr_2 \ . \tag{3.6}$$

The last term in this expression is reminiscent of the quadratic correction in the first order NMT correction to MS$X\alpha$ theory,[6] but it is fundamentally different in that the approximate wave function responding to the approximate potential [Eq. (2.7)] sees no large localized unphysical forces such as those associated with the MT interfaces. Thus, in principle, $\Delta\rho$ can be spread out to the point that this term becomes quite small. Evidence that this can be practically achieved is given in Sec. V.

If both $\tilde{U}_c$ and $\tilde{\tilde{U}}_c$ can be calculated, as easily can be done in a Gaussian method, then the most accurate approximation to U_c results from minimizing

$$D' = \int \Delta\rho(1)\,\Delta\rho(2)/r_{12}\,dr_1\,dr_2$$
$$= \int (\rho(1) - \tilde{\rho}(1))(\rho(2) - \tilde{\rho}(2))/r_{12}\,dr_1\,dr_2 \ , \tag{3.7}$$

which is a positive-definite quantity. Requiring that this be stationary together with the normalization constraint Eq. (3.2) results in a fit given by Eq. (3.4) with

$$t_i = \int \rho(1)f_i(2)/r_{12}\,dr_1\,dr_2 \ ,$$

and

$$S_{ij} = \int f_i(1)f_j(2)/r_{12}\,dr_1\,dr_2 \ . \tag{3.8}$$

This alternate fitting procedure means that barring second order effects brought about through self-consistency, an incomplete CDB and a neglect of D' in U_c will result in an EXα that bounds the true EXα from below (not from above as results from an incomplete OB).

Further insight into the error term Eq. (3.7) can be gained from elementary electrostatics. The self-energy of a charge distribution is equal to the energy of the generated (static) electric fields. Thus,

$$D' = (1/4\pi)\int |\mathbf{E}(1) - \tilde{\mathbf{E}}(1)|^2\,dr_1 \ ,$$

where

$$E(1) = \nabla \int \rho(2)/r_{12} d\mathbf{r}_2 ,$$

with a similar equation for $\tilde{E}$. Therefore, Eqs. (3.4) and (3.8) are equivalent to a least squares fit of the electronic electric fields. In other words, fitting the electric field generated by the electrons is better than fitting either the electronic density or the potential generated by that density in the sense that so doing minimizes the quadratic in $\Delta\rho$ contribution to U_c and hence to $EX\alpha$.

There is a computational advantage to using Eq. (3.8). Namely, the t_i of that equation and $\bar{V}_c$ share a common set of elemental integrals which need only be computed once.

In Sec. V we will investigate the relative merits of Eq. (3.3) vs. Eq. (3.8) subject to the approximation

$$U_c \simeq 2\bar{U}_c - \bar{\bar{U}}_c . \tag{3.9}$$

IV. EXCHANGE

In the region of space nearest any given nucleus the sampling points and weights were determined as follows. The radial distribution consisted of every tenth point of the Herman—Skillman[24] mesh.[25] This series was terminated when the magnitudes of all the basis functions fell below a predetermined tolerance.[26] The angular mesh consisted of the twelve vertices of a regular icosahedron (weighted equally), specifically

$$x = \pm\sqrt{(\sqrt{5}+1)/2\sqrt{5}}$$

$$y = \pm\sqrt{(\sqrt{5}-1)/2\sqrt{5}}$$

$$z = 0 ,$$

and the three cyclic permutations of these coordinates. Viewed as an numerical angular integration scheme, this mesh is accurate through fifth order spherical harmonics.[27] The combined weights were chosen to be the volume nearest each point. For diatomic molecules reflection symmetry was used to reduce the angular grid to 5 points. Typically this procedure gave 150 points per inequivalent atom.

This distribution of sample points was chosen over a more uniform distribution[7] in order that the method not be limited to frozen core calculations. These rules are easily generalizable to yield larger numbers of sampling points, but they are sufficient empirically. Two factors contribute to the small number of points needed to fit $\rho^{1/3}$ (relative to the number needed in a similar DVM calculation). First, the exchange is a rather small component of the total energy. Second and more important is the smoothing power of the cube root function— $\rho^{1/3}$ is much easier to fit than ρ.

Several constraints on the fit to $\rho^{1/3}$ have been investigated. The constraint

$$\int (\bar{\rho}^{1/3})^3 dr = N_e ,$$

is cubic in the b_i of Eq. (2.14), but this expression can be expanded in a Taylor series about each previous fit.

Neglecting quadratic and higher order terms in the changes in the b_i gives a linear constraint, and iterating the resultant constrained fit to V_x only once per SCF cycle leads to a method that is overall as rapidly convergent as one without a constraint. The number of integrals that must be computed and stored to effect this constraint is large ($\sim N^3$) but manageable. A more economical constraint is

$$\sum_i w_i [\bar{\rho}(\mathbf{r}_0)^{1/3}]^4 = \sum_i w_i \rho(\mathbf{r}_i)\bar{\rho}(\mathbf{r}_i)^{1/3} \left(\simeq \int \rho(\mathbf{r}_i)^{4/3} d\mathbf{r} \right) .$$

The parenthetical equality indicates the motivation behind this constraint which is to improve the reliability of the calculation of the exchange term in the $X\alpha$ total energy expression. However, neither constraint has had any significant effect on the calculations performed to date.

An avenue for possible future investigation results from an analogy with the treatment of V_c presented in the previous section. Requiring the following expression for the exchange energy,

$$U_x/C = \frac{4}{3} \int \rho(\mathbf{r}_1)\bar{\rho}(\mathbf{r}_1)^{1/3} d\mathbf{r}_1 - \frac{1}{3} \int [\bar{\rho}(\mathbf{r}_1)^{1/3}]^4 d\mathbf{r}_1 , \tag{4.1}$$

be stationary with respect to variations of the fit to $\rho^{1/3}$ results in an analytic expression for the coefficients b_i in Eq. (2.14):

$$\int \rho(\mathbf{r}_1) g_i(\mathbf{r}_i) d\mathbf{r}_i = \sum_{j,k,l} b_j b_k b_l$$

$$\times \int g_i(\mathbf{r}_1) g_j(\mathbf{r}_1) g_k(\mathbf{r}_1) g_l(\mathbf{r}_1) d\mathbf{r}_1 . \tag{4.2}$$

The use of Eqs. (4.1)—(2) in addition to yielding an $X\alpha$ method that is variational in the orbital and both fitting bases would eliminate the need for any multidimensional fitting or numerical integration grid, but at the cost of an $\sim N^4$ method.

V. DISCUSSION

The calculated lowest lying $X\alpha$ states for atomic nickel are given in Table I. Nonspin-polarized calculations are not included due to the lack of a direct interpretation in terms of multiplet averages.[28] A description of multiplets within a single configuration is beyond a one-electron model. Thus, in the rightmost columns of Table I we compare averages over the relevant experimental multiplets[29] with the $X\alpha$ quantities. (Within a configuration the $X\alpha$ singlet—triplet separation has been computed based on the analysis of Ziegler and Rauk.[30]) From the table $X\alpha$ averages for nickel are in slight disagreement with experiment,[29] which cannot be substantially improved by varying α.[31] (Unless otherwise noted we have used the α_{HF} values of Schwartz[32]).

Details of the calculations are as follows. The (14s, 9p, 5d) GTO OB of Wachters[33] was augmented to (14, 10, 6) with diffuse functions.[34] An earlier technique[22] of obtaining the exponents of the auxiliary bases via nonlinear least squares fit to the Herman—Skillman nickel charge density[24] and its cube root was abandoned due to numerical instabilities associated with large numbers of pa-

TABLE I. The energies (in hartrees) of configurations of atomic nickel in the Xα model.

Configuration	Total Xα energy		Energy corrections		Relative separations	
	Numerical	LCGTO[a]	Eq. (3.8)	Eq. (3.3)	Xα	Experiment[29]
$3d^8 4s^2$ Singlet	-1506.813	-1506.762	0.008	0.094	0.153	0.083
$3d^8 4s^2$ Triplet	-1506.859	-1506.805	0.008	0.094	0.061	0.021
$3d^9 4s$ Singlet	-1506.912	-1506.856	0.013	0.129	0.016	0.012
$3d^9 4s$ Triplet	-1506.920	-1506.863	0.013	0.130	···	···
$3d^{10}$ Singlet	-1506.861	-1506.811 (2)	0.016	0.168	0.059	0.064

[a]In parentheses is the last digit using Eq. (3.3) rather than Eq. (3.8).

rameters.[35] Instead the CDB consisted of the diagonal (in OB functions) terms occurring in Eq. (2.3) (i.e., the exponents were doubled). The XB exponents were the CDB exponents reduced by two-thirds. The spherically symmetric d-type auxiliary functions greatly facilitate the positioning of the density shoulders associated with the shell structure of the nickel atom. The g-type functions were found superfluous and discarded.

The third set of columns in Table I give

$$\Delta E = \tilde{U}_c - \tilde{\tilde{U}}_c = \frac{1}{2} \int \tilde{\rho}(1) \, \Delta\rho(2)/r_{12} \, dr_1 dr_2$$

which corrects $\tilde{U}_c$ and the total energy through first order in $\Delta\rho$. As can be seen, these corrections are an order to magnitude smaller if the electric field rather than the density is fit. Detailed comparisons of the two fitting procedures revealed: (1) Eq. (3.8) yields one-electron eigenvalues uniformly 0.007 hartree higher and total energies uniformly 0.0006 hartree higher. (2) The linear coefficients for fitting the charge density [a_i in Eq. (2.12)] varied by as much as a factor of three between the two calculations. (The b_i were within 10% of each other.) Therefore, we conclude the corrected Xα energies are independent of the auxiliary bases to the 0.001 hartree level. The uniform 0.05 hartree increase over numerical results is due to OB incompleteness and is comparable to the 0.08 hartree found by Wachters[33] in HF calculations.

Table II contains results of various H_2 calculations. The OB exponents were obtained from Huzinaga's[36] 4 to 6 term expansion of an STO,

$$e^{-\lambda r} = \sum_i c_i (2\beta_i/\lambda^2)^{3/4} e^{-\beta_i r^2} \ . \tag{5.1}$$

The auxiliary functions were obtained in the manner described for atomic nickel augmented with a p-type and a bond-centered function.

Again we conclude the corrected total energies are independent of the auxiliary bases to the accuracy quoted by virtue of the agreement between the two fitting procedures. As is the case with HF, a scaling parameter λ slightly larger than 1.0 gives a lower total energy.

In our studies of N_2, we use Eq. (3.8) exclusively. Table III contains the results of a study of the effects of OB size and composition. The first group of entries in that table employ the ($5p$, $2p$) through ($11s$, $6p$) atomic

GTO bases of van Duijneveldt[38] without polarization functions. The corresponding auxiliary bases were chosen in the manner described above for calculations on atomic nickel and H_2 with the exception that five p type and three d type (each divided into a d_{zz} and a d_{rr} component) auxiliary functions were found sufficient. Since the auxiliary bases grew with the OB and the energy decreases with the more extend calculations, it is apparent that OB incompleteness dominates for these calculations of up to approximately double zeta quality. The remainder of these calculations explored adding d-type polarization functions to the OB (without corresponding increases to the auxiliary bases). A similar but somewhat more extensive HF study using an STO OB was performed by Cade, Sales, and Wahl.[37] We (Ref. 37) obtained incremental energy lowerings in hartrees of 0.0258 (0.0521) via the addition of a $\pi_u 3d$ orbital, 0.0139 (0.0278) via $\sigma_g 3d$, and 0.0016 (0.0013) via $\pi_u 3d'$ and $\pi_u 3d''$. Most likely, our smaller lowerings accompanying the addition of an initial d function are due to our larger s and p basis, and our slower convergence is due to the use of a GTO rather than an STO basis. From this experience we expect that adding f functions would lower the energy by approximately one-half of the 0.0036 hartree found in Ref. 37. Exponent optimization could yield an additional lowering of around the 0.0031 hartree obtained in that work by optimizing their ($12\sigma_g$, $8\sigma_u$, $6\pi_u$) basis.

Table IV shows the effects of deleting classes of functions from both auxiliary basis sets. The nonSCF results were obtained using the one-electron eigenfunctions found in the SCF calculation using the entire basis sets. The SCF quantities are the converged results of calculations using the truncated bases. The nonSCF U_c is rigorously variational, and the nonSCF EXα would have been variational if only charge density auxiliary functions

TABLE II. The basis dependence of the Xα energy (in hartrees) of molecular hydrogen at an internuclear separation of 1.4 bohr.

Basis[36] (s, p)	λ	EXα	ΔE	
			Eq. (3.8)	Eq. (3.3)
(4,1)	1.0	1.1334	0.0024	
(5,1)	1.0	1.1348	0.0010	0.0051
(5,1)	1.2	1.1349	0.0014	0.0038
(6,1)	1.0	1.1352	0.0001	0.0004
(6,1)	1.2	1.1353	-0.0003	-0.0049

TABLE III. Orbital basis dependencies of $X\alpha$ quantities for $N_2(X\,^1\Sigma_g^+)$ at $z = 2.07\ a_0$.

Atomic basis[38] (s,p)	Molecular basis (σ_g, σ_u, π_u)	E	ΔE	T	$-V/T$	$\epsilon 1\sigma_g$	$\epsilon 1\sigma_u$	$\epsilon 2\sigma_g$	$\epsilon 2\sigma_u$	$\epsilon 1\pi_u$	$\epsilon 3\sigma_g$
				(Hartree Atomic Units)							
(5,2)	(7,7,2)	-108.4840	0.0219	108.1275	2.00330	-14.2123	-14.2133	-1.0819	-0.4336	-0.3695	-0.2821
(7,3)	(10,10,3)	-109.0922	0.0232	108.9873	2.00096	-14.1472	-14.1458	-1.1007	-0.4740	-0.4206	-0.3659
(8,4)	(12,12,4)	-109.1614	0.0005	109.2891	1.99883	-14.1245	-14.1232	-1.0851	-0.4706	-0.4308	-0.3597
(9,5)	(14,14,5)	-109.1992	0.0008	109.2544	1.99950	-14.1292	-14.1278	-1.0890	-0.4740	-0.4351	-0.3642
(11,6)	(17,17,6)	-109.2135	-0.0052	109.2287	1.99986	-14.1364	-14.1350	-1.0930	-0.4808	-0.4397	-0.3730
(11,6)a	(17,17,7)a	-109.2493	0.0037	109.1861	2.00058	-14.1222	-14.1209	-1.0534	-0.4843	-0.4337	-0.3723
(9,5)	(15,14,7)b	-109.2474	0.0065	109.1747	2.00067	-14.1126	-14.1112	-1.0417	-0.4813	-0.4246	-0.3708
(11,6)b	(18,17,7)b	-109.2632	0.0031	109.1772	2.00078	-14.1163	-14.1149	-1.0428	-0.4857	-0.4285	-0.3744
(12,7)	(20,19,8)b	-109.2649	0.0108	109.1715	2.00086	-14.1177	-14.1164	-1.0489	-0.4878	-0.4296	-0.3780
(13,8)	(22,21,9)b	-109.2645	0.0078	109.1716	2.00085	-14.1180	-14.1167	-1.0465	-0.4879	-0.4295	-0.3784
(11,6)c	(18,17,8)c	-109.2648	0.0029	109.1689	2.00088	-14.1157	-14.1143	-1.0405	-0.4857	-0.4272	-0.3745
(11,6)d	(18,17,9)d	-109.2655	0.0025	109.1702	2.00087	-14.1151	-14.1138	-1.0397	-0.4857	-0.4270	-0.3745

aIncludes a $\pi_u 3d$ basis function.
bIncludes $\pi_u 3d$ and $\sigma_g 3d$ basis functions.
cIncludes $\pi_u 3d$, $\pi_u 3d'$, and $\sigma_g 3d$ basis functions.
dIncludes $\pi_u 3d$, $\pi_u 3d'$, $\pi_u 3d''$, and $\sigma_g 3d$ basis functions.

TABLE IV. Charge density and exchange basis dependencies of $X\alpha$ quantities for $N_2(X\,^1\Sigma_g^+)$ at $z = 2.07\ a_0$.

Auxiliary[a] Bases	EXα		U_c		U_x	
	NonSCF	SCF	NonSCF	SCF	NonSCF	SCF
(11,5,3,3,2)	-109.2655	-109.2655	75.4512	75.4512	-13.2243	-13.4243
(11,5,0,3,2)	-109.2659	-109.2659	74.4509	75.4512	-13.4245	-13.4245
(11,3,3,3,2)	-109.2659	-109.2659	75.4504	75.4545	-13.4241	-13.4248
(11,0,3,3,2)	-109.2652	-109.2653	75.4496	75.4555	-13.4225	-13.4236
(11,5,3,3,0)	-109.2676	-109.2676	75.4497	75.4512	-13.4250	-13.4253
(11,5,0,0,2)	-109.2679	-109.2680	75.4495	75.4533	-13.4250	-13.4256
(11,0,0,3,0)	-109.2836	-109.2792	75.4450	75.3971	-13.4362	-13.4179

aThis notation is $(s, p_z, d_{zz}, d_{rr}, \text{bond-centered } s)$.

had been deleted. The (approximate) U_c and U_x values indicate that the error associated with an incomplete XB and an incomplete CDB become comparable if they are the same size and have the same nonspherical and off-center flexibility. It would appear that off-center functions are more important for fitting the exchange, whereas the higher angular momentum functions are more important for the CDB. From this table we conclude that the addition of any further auxiliary function will raise the energy less than 0.0001 hartree.

The lowest entry of Table IV results from deleting all but atom-centered spherical auxiliary functions and has an error of only 0.0137 hartree. Comparing this with Table III, we conclude that only if polarization functions are included in the OB is the use of directional auxiliary functions warranted. Finally, from these tables and the fact that the two variational principles associated with OB and CDB basis incompleteness are in opposition, we believe the lowest entry of Table III (highest of Table IV) give EXα for N_2 at an internuclear separation of 2.07 bohr to within 0.005 hartree or 0.2 eV.

In Table V several quantities derivable from the total $X\alpha$ energy are compared with experiment (using at least 6 points on the potential energy curves). We believe that they are within 5% of the exact $X\alpha$ quantities. The H_2 data are in agreement with other NMT$X\alpha$ calculations.[41-43] Our results for N_2^+ and N_2 are in general agreement with recent DVM calculations.[20,37,44] We will postpone a detailed comparison with other one-electron methods and theories until we have completed our stud-

TABLE V. Comparison with experiment of some total $X\alpha$ energy dependent quantities.

Molecule	$X\alpha$			Experiment[37,39,40]		
	$R_e(a_0)$	ω_e (cm^{-1})	D_e (eV)[a]	$R_e(a_0)$	ω_e(cm^{-1})	D_e (eV)[a]
$H_2\ ^1\Sigma_g$	1.41	4625	3.69	1.40	4400	4.48
$N_2\ ^1\Sigma_g$	2.04	2513	9.41	2.07	2358	9.76
$N_2^+\ ^2\Sigma_g$	2.08	2440	15.3	2.11	2207	15.6
$N_2^+\ ^2\Pi_u$	2.18	1986	17.2	2.22	1903	17.0
$N_2^+\ ^2\Sigma_u$	1.98	2782	18.4	2.03	2420	18.8
$H_2\ (\alpha = 0.7)$	1.46	4155	3.58	1.40	4400	4.48
$N_2\ (\alpha = 0.7)$	2.07	2443	9.24	2.07	2358	9.76

aFor N_2^+ the vertical ionization potentials at an internuclear separation of 2.07 a_0 are given.

ies of additional first-row diatomics including F_2 which is a more sensitive test case.[45]

VI. CONCLUSIONS

We have discussed some of the errors in various $X\alpha$ methods as applied. An analysis of fitting procedures lead us to a variant of the method of Sambe and Felton with which reliable LCAO$X\alpha$ total energies can be obtained using finite basis sets. If the three basis sets (OB, CDB, and XB) are of comparable size and angular flexibity the error in the total $X\alpha$ energy is dominated by the incompleteness of the OB. In any event, there are two variational principles at work so that, apart from self-consistency effects, increasing the OB will lower the energy and increasing the CDB and XB will raise it.

ACKNOWLEDGMENT

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