

# A gradient search method for orbital-dependent density functional calculations

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We describe a gradient search method appropriate for electronic structure problems where the energy functionals are explicitly orbital-dependent. The ground state is found by minimizing the total energy with respect to the scalar and vector potentials that enter the Kohn-Sham equations. The method is exact in principle and provides an alternative to the conventional procedure which requires the numerical solution of an integral equation. We demonstrate the method for atoms with spherical effective potentials using (i) a local spin-density functional which does not depend explicitly on the orbitals and (ii) an exact exchange functional which does depend explicitly on the orbitals.

## I. INTRODUCTION

The Kohn-Sham form of density-functional theory is often the most practical method for calculating the electronic structure of materials. This is especially true for the local-density approximation (LDA) and its variants including the local-spin-density approximation and generalized gradient approximations. In these approximations, the exchange-correlation potential is easily calculated from the functional derivative of the exchange-correlation energy with respect to the density. However, many energy functionals designed to improve on the LDA are not explicit functionals of the density and the functional derivative can not be evaluated so easily. A notable example is the exact-exchange functional.<sup>1-4</sup> Functionals with self-interaction corrections<sup>5</sup> also fall into this category.

In all of these cases, the functionals of interest depend explicitly on the non-interacting Kohn-Sham orbitals. This is sufficient to guarantee that they are all legitimate density functionals because the Hohenberg-Kohn theorem<sup>9</sup> asserts that the non-interacting Kohn-Sham orbitals are implicitly functionals of the density. Kohn-Sham exchange-correlation potentials for these energy functionals exist but are difficult to evaluate. To solve this problem, one exploits the fact that the energy is stationary with respect to the exchange-correlation scalar potential at the energy minimum. This is the so-called optimized effective potential (OEP) method.<sup>1</sup> The most common method for finding the potential is by solving an integral equation,<sup>2-5</sup> but it is also possible to find the potential by directly minimizing the energy with respect to the potential.<sup>6-8</sup>

This paper makes two contributions to the issues outlined above. First, we generalize conventional OEP and treat the energy as an explicit functional of an effective scalar potential  $V_{\text{HXC}}(\mathbf{r})$  and an effective vector potential  $\mathbf{A}_{\text{HXC}}(\mathbf{r})$ . The latter will be needed when orbital-dependent functionals are applied to the current-density-functional theory of Vignale and Rasolt.<sup>10</sup> Second, we describe a gradient search algorithm to find the energy minimum in the space of these four functions. We present a numerical test of this algorithm for the case of an effective scalar potential.

The plan of this paper is as follows. Section II reviews some basic results and establishes our notation. Section III describes our new method. Section IV describes an application to spherical atoms for two choices of energy functional. Section V summarizes our results.

## II. BACKGROUND

We begin by deriving a few well-known results from conventional charge- and current-density functional theory. For an electronic system coupled to external electric and magnetic fields, the total energy to be minimized is

$$E = \int d^3r \sum_n \phi_n^*(\mathbf{r}) \hat{T} \phi_n(\mathbf{r}) + E_{\text{HXC}} + \sum_\alpha \int d^3r A_{\text{EXT}}^\alpha(\mathbf{r}) j^\alpha(\mathbf{r}). \quad (1)$$

In this formula,  $\hat{T}$  is the kinetic energy operator and  $\phi_n(\mathbf{r})$  is a one-electron (Kohn-Sham) orbital for a non-interacting system.  $E_{\text{HXC}}$  is the sum of the Hartree and exchange-correlation energy functionals. The Hartree part of  $E_{\text{HXC}}$  is an explicit functional of the density. The exchange-correlation part of  $E_{\text{HXC}}$  is guaranteed by the Hohenberg-Kohn theorem to be a functional of the charge and paramagnetic current density. However this dependence need not be

explicit. In particular, it can be implicit through an explicit dependence of the functional on the Kohn-Sham orbitals. Such is the case for the exact exchange functional. The last term in Eq. (1)

$$\sum_{\alpha} \int d^3r A_{\text{EXT}}^{\alpha}(\mathbf{r}) j^{\alpha}(\mathbf{r}) = \int d^3r \left[ V_{\text{EXT}}(\mathbf{r}) + \frac{e A_{\text{EXT}}^2(\mathbf{r})}{2mc^2} \right] \rho(\mathbf{r}) - \frac{1}{c} \int d^3r \mathbf{A}_{\text{EXT}}(\mathbf{r}) \cdot \mathbf{j}(\mathbf{r}), \quad (2)$$

describes the coupling between the charged particles and an external scalar and vector potential in the usual way. The charge and current densities are written in terms of the Kohn-Sham orbitals as

$$j^{\alpha}(\mathbf{r}) = \frac{1}{2} \sum_n \phi_n^*(\mathbf{r}) \hat{j}^{\alpha} \phi_n(\mathbf{r}) + h.c. \quad (3)$$

where  $\hat{j}^0 = e$ ,  $\hat{\mathbf{j}} = -i(e/m)\nabla$ , and the sum (here and below) is over all occupied orbitals. These orbitals are solutions to the anti-commutator form of the noninteracting Kohn-Sham equation<sup>10</sup>

$$\hat{H}_{\text{KS}} \phi_n(\mathbf{r}) = \left\{ \hat{T} + \sum_{\alpha} \frac{1}{2} [\hat{j}^{\alpha}, A_{\text{EXT}}^{\alpha}(\mathbf{r}) + A_{\text{HXC}}^{\alpha}(\mathbf{r})]_{+} \right\} \phi_n(\mathbf{r}) = e_n \phi_n(\mathbf{r}). \quad (4)$$

where  $A_{\text{HXC}}^{\alpha}(\mathbf{r})$  are effective potentials. At the minimum of Eq. (1) these orbitals reproduce the charge and current densities of the interacting system.

The minimum of Eq. (1) is found with respect to variations in  $A_{\text{HXC}}^{\alpha}(\mathbf{r})$ . This is done by first eliminating the kinetic energy from Eq. (1) in favor of  $\hat{H}_{\text{KS}}$  using Eq. (4). This gives

$$E = \langle \text{KS} | \hat{H}_{\text{KS}} | \text{KS} \rangle + E_{\text{HXC}} - \sum_{\alpha} \int d^3r A_{\text{HXC}}^{\alpha}(\mathbf{r}) j^{\alpha}(\mathbf{r}) \quad (5)$$

where  $|\text{KS}\rangle$  is the Kohn-Sham ground state. We now compute the gradient of  $E$  with respect to  $A_{\text{HXC}}^{\alpha}(\mathbf{r})$ . Using the Hellmann-Feynman theorem, the first term gives

$$\frac{\delta}{\delta A_{\text{HXC}}^{\alpha}(\mathbf{r})} \langle \text{KS} | \hat{H}_{\text{KS}} | \text{KS} \rangle = \langle \text{KS} | \frac{\delta \hat{H}_{\text{KS}}}{\delta A_{\text{HXC}}^{\alpha}(\mathbf{r})} | \text{KS} \rangle = j^{\alpha}(\mathbf{r}). \quad (6)$$

This term cancels with one of the two terms produced when the gradient operates on the last term in Eq. (5) and we are left with

$$\frac{\delta E}{\delta A_{\text{HXC}}^{\alpha}(\mathbf{r})} = \frac{\delta E_{\text{HXC}}}{\delta A_{\text{HXC}}^{\alpha}(\mathbf{r})} - \sum_{\alpha} \int d^3r' A_{\text{HXC}}^{\alpha}(\mathbf{r}') \frac{\delta j^{\alpha}(\mathbf{r}')}{\delta A_{\text{HXC}}^{\alpha}(\mathbf{r})} \quad (7)$$

The left side of this equation is zero when the energy is a minimum so we get

$$\frac{\delta E_{\text{HXC}}}{\delta A_{\text{HXC}}^{\alpha}(\mathbf{r})} = \sum_{\alpha} \int d^3r' A_{\text{HXC}}^{\alpha}(\mathbf{r}') \frac{\delta j^{\alpha}(\mathbf{r}')}{\delta A_{\text{HXC}}^{\alpha}(\mathbf{r})}. \quad (8)$$

Since  $E_{\text{HXC}}$  is a functional of the charge and current densities we have from the chain rule

$$\sum_{\alpha} \int d^3r' \frac{\delta E_{\text{HXC}}}{\delta j^{\alpha}(\mathbf{r}')} \frac{\delta j^{\alpha}(\mathbf{r}')}{\delta A_{\text{HXC}}^{\alpha}(\mathbf{r})} = \sum_{\alpha} \int d^3r' A_{\text{HXC}}^{\alpha}(\mathbf{r}') \frac{\delta j^{\alpha}(\mathbf{r}')}{\delta A_{\text{HXC}}^{\alpha}(\mathbf{r})}. \quad (9)$$

Therefore, at the minimum we have the standard result

$$A_{\text{HXC}}^{\alpha}(\mathbf{r}) = \frac{\delta E_{\text{HXC}}}{\delta j^{\alpha}(\mathbf{r})} \quad (10)$$

Unfortunately, the formal definition of  $A_{\text{HXC}}^{\alpha}$  in Eq. (10) is not very useful for practical calculations when  $E_{\text{HXC}}$  is not an explicit function of the charge density and/or the current density. One way to make progress is to regard Eq. (8) as an integral equation for  $A_{\text{HXC}}^{\alpha}(\mathbf{r})$  to be solved, *e.g.* by numerical matrix inversion. This is a non-trivial task which, to our knowledge, has been attempted only when the vector potential is absent<sup>1-5</sup>. In that case, Eq. (8) reduces to

$$\frac{\delta E_{\text{HXC}}}{\delta V_{\text{HXC}}(\mathbf{r})} = \int d^3r' V_{\text{HXC}}(\mathbf{r}') \frac{\delta \rho(\mathbf{r}')}{\delta V_{\text{HXC}}(\mathbf{r})}. \quad (11)$$

More interesting cases where magnetic fields (either external or internal) are present appear to be prohibitively difficult by this method. For this reason, we have developed an alternative.

### III. THE GRADIENT SEARCH METHOD

Our proposal is to use  $A_{\text{HXC}}^\alpha(\mathbf{r})$  as the independent variable(s) in a gradient search algorithm to find the minimum of  $E$ . This requires a practical scheme to compute the right hand side of Eq. (7) or its equivalent. For this purpose, it turns out to be convenient to compute gradients of

$$\begin{aligned}
E' &= \int d^3r \sum_n \phi_n^*(\mathbf{r}) \hat{T} \phi_n(\mathbf{r}) + \sum_\alpha \int d^3r A_{\text{EXT}}^\alpha(\mathbf{r}) j^\alpha(\mathbf{r}) + E_{\text{HXC}} \\
&\quad - \int d^3r \sum_n \left[ g_n^*(\mathbf{r}) \left( \hat{H}_{\text{KS}} - e_n \right) \phi_n(\mathbf{r}) + \text{c.c.} \right] \\
&\quad - \sum_n \lambda_n \left( \int d^3r |\phi_n(\mathbf{r})|^2 - 1 \right)
\end{aligned} \tag{12}$$

with respect to the *independent* variable set  $\{g_n^*(\mathbf{r}), \lambda_n, \phi_n^*(\mathbf{r}), e_n, A_{\text{HXC}}^\alpha(\mathbf{r})\}$ . The straightforward result is

$$\frac{\partial E'}{\partial g_n^*(\mathbf{r})} = (e_n - \hat{H}_{\text{KS}}) \phi_n(\mathbf{r}) \tag{13}$$

$$\frac{\partial E'}{\partial \lambda_n} = 1 - \int d^3r |\phi_n(\mathbf{r})|^2 \tag{14}$$

$$\frac{\partial E'}{\partial \phi_n^*(\mathbf{r})} = \left\{ \hat{T} + \sum_\alpha \frac{1}{2} [\hat{j}^\alpha, A_{\text{EXT}}^\alpha(\mathbf{r})]_+ \right\} \phi_n(\mathbf{r}) + \frac{\partial E_{\text{HXC}}}{\partial \phi_n^*(\mathbf{r})} - \lambda_n \phi_n(\mathbf{r}) - (\hat{H}_{\text{KS}} - e_n) g_n(\mathbf{r}) \tag{15}$$

$$\frac{\partial E'}{\partial e_n} = \int d^3r [g_n^*(\mathbf{r}) \phi_n(\mathbf{r}) + \phi_n^*(\mathbf{r}) g_n(\mathbf{r})] \tag{16}$$

$$\frac{\partial E'}{\partial A_{\text{HXC}}^\alpha(\mathbf{r})} = - \sum_n \left( g_n^*(\mathbf{r}) \hat{j}^\alpha \phi_n(\mathbf{r}) + \text{c.c.} \right). \tag{17}$$

Note that the Kohn-Sham equations and normalized eigenfunctions arise when we minimize with respect to the Lagrange functions  $g_n^*(\mathbf{r})$  and  $\lambda_n$ . Similarly, minimization with respect to  $\phi_n^*(\mathbf{r})$  and  $e_n$  together determine  $g_n^*(\mathbf{r})$ , which in turn is needed in Eq. (17) to find the gradient of  $E'$  with respect to  $A_{\text{HXC}}^\alpha(\mathbf{r})$ .

All the gradients above are zero when the total energy achieves its minimum value. In principle, the non-zero gradient values away from the minimum could be used in a multi-variable search algorithm to find the energy minimum. Alternatively, we are free to search for the minimum in a subspace where any number of the gradients are strictly zero. In particular, if we restrict the search to the subspace where all the gradients are always zero except for  $\partial E' / \partial A_{\text{HXC}}^\alpha(\mathbf{r})$ , we can eliminate the kinetic energy in Eq. (15) (set to zero) and rewrite it in terms of  $H_{\text{KS}}$  as before. The result is

$$(\hat{H}_{\text{KS}} - e_n) g_n(\mathbf{r}) = \frac{\partial E_{\text{HXC}}}{\partial \phi_n^*(\mathbf{r})} - \sum_\alpha \frac{1}{2} [\hat{j}^\alpha, A_{\text{HXC}}^\alpha(\mathbf{r})]_+ \phi_n(\mathbf{r}) - \lambda_n \phi_n(\mathbf{r}). \tag{18}$$

This is an inhomogeneous Schrödinger equation for  $g_n(\mathbf{r})$ . The partial derivative  $\partial E_{\text{HXC}} / \partial \phi_n^*(\mathbf{r})$  is known because  $E_{\text{HXC}}$  is an explicit functional of the orbitals.  $A_{\text{HXC}}^\alpha(\mathbf{r})$  is the independent variable for the gradient search so it remains only to determine  $\lambda_n$ . To do so, we multiply Eq. (18) on the left by  $\phi_n^*(\mathbf{r})$  and integrate over all space. This gives

$$\lambda_n = \int d^3r \phi_n^*(\mathbf{r}) \left( \frac{\partial E_{\text{HXC}}}{\partial \phi_n^*(\mathbf{r})} - \sum_\alpha \frac{1}{2} [\hat{j}^\alpha, A_{\text{HXC}}^\alpha(\mathbf{r})]_+ \phi_n(\mathbf{r}) \right). \tag{19}$$

in terms of known quantities.

Notice that Eq. (18) leaves the overlap of  $g_n(\mathbf{r})$  with  $\phi_n(\mathbf{r})$  undetermined. On the other hand, setting Eq. (16) to zero demands that this overlap must be purely imaginary and a purely imaginary overlap makes no contribution to the right side of Eq. (17). Therefore, for convenience, the constraint obtained by setting Eq. (16) to zero may be replaced by

$$\int d^3r g_n^*(\mathbf{r}) \phi_n(\mathbf{r}) = 0. \tag{20}$$

Our procedure is then as follows: (i) make an educated guess for  $A_{\text{HXC}}^\alpha(\mathbf{r})$ ; (ii) calculate  $\phi_n(\mathbf{r})$  from the Kohn-Sham equations; (iii) calculate  $g_n(\mathbf{r})$  from Eq. (18) subject to the constraint Eq. (20); (iv) calculate the gradient Eq. (17) and use it in a minimization scheme to update  $A_{\text{HXC}}^\alpha(\mathbf{r})$ ; (v) go back to step (ii) and repeat until the minimum of  $E$  is reached.

This procedure is related to two previous methods. Both Bulgac et al.<sup>7</sup> and Fritsche and Yuan<sup>8</sup> parameterize the potential and minimize the energy with respect to these parameters. Fritsche and Yuan use a minimization method that does not use analytic gradients. They use their method to compute energies within the exact exchange approximation for spherical atoms. In Section IV, we compare our results to theirs. Bulgac et al. use a gradient-based method very similar to what we describe here, except that the gradient is computed with respect to the parameters for the potential. They apply their method to jellium models of clusters.

For many problems, it is easiest to solve the Kohn-Sham equations using a basis set. For example,

$$g_n(\mathbf{r}) = \sum_{m \neq n} \phi_m(\mathbf{r}) \int d^3 r' \phi_m^*(\mathbf{r}') g_n(\mathbf{r}'). \quad (21)$$

is an expansion of  $g_n(\mathbf{r})$  in terms of the Kohn-Sham orbitals themselves. Notice that the sum here includes both occupied and unoccupied orbitals. The exclusion of the  $m = n$  term guarantees that Eq. (21) satisfies Eq. (20). Using Eq. (21), the exact solution for  $g_n(\mathbf{r})$  is found trivially from Eq. (18) to be

$$g_n(\mathbf{r}) = \sum_{m \neq n} \frac{\phi_m(\mathbf{r})}{e_m - e_n} \int d^3 r' \phi_m^*(\mathbf{r}') \left( \frac{\partial E_{\text{HXC}}}{\partial \phi_n^*(\mathbf{r}')} - \sum_{\alpha} \frac{1}{2} [\hat{j}^\alpha, A_{\text{HXC}}^\alpha(\mathbf{r}')]_+ \phi_n(\mathbf{r}') \right).$$

Using this result in the expression for the derivative of  $E_{\text{HXC}}$  in Eq. (17) gives

$$\begin{aligned} \frac{\partial E}{\partial A_{\text{HXC}}^\alpha(\mathbf{r})} &= \sum_n \sum_{m \neq n} \frac{\phi_n^*(\mathbf{r}) \hat{j}^\alpha \phi_m(\mathbf{r})}{e_m - e_n} \\ &\int d^3 r' \phi_m^*(\mathbf{r}') \left( \frac{\partial E_{\text{HXC}}}{\partial \phi_n^*(\mathbf{r}')} - \sum_{\alpha} \frac{1}{2} [\hat{j}^\alpha, A_{\text{HXC}}^\alpha(\mathbf{r}')]_+ \phi_n(\mathbf{r}') \right) + \text{c.c.} \end{aligned} \quad (22)$$

This equation is identical to Eq. (7). We derived it variationally, but it can also be obtained from perturbation theory.

#### IV. APPLICATION TO SPHERICAL ATOMS

In this section, we demonstrate our method for free atoms using two choices for the total energy functional. For simplicity, we put  $\mathbf{A}_{\text{HXC}}(\mathbf{r}) = 0$  and restrict ourselves to an effective spin-dependent scalar potential  $V_{\text{HXC}\sigma}(r)$  that is spherically symmetric. In that case, the Kohn-Sham orbitals take the form

$$\phi_{n\ell m\sigma}(r, \theta, \phi) = \phi_{n\ell\sigma}(r) Y_{\ell m}(\theta, \phi). \quad (23)$$

Despite the fact that the effective potential is spherically symmetric, the resulting density

$$\rho_\sigma(r, \theta) = \sum_{\ell} \rho_{\ell\sigma}(r) Y_{\ell 0}(\theta, \phi), \quad (24)$$

need not be. Here, the different contributions to the density are

$$\rho_{\ell\sigma}(r) = \sum_{n\ell'm} |\phi_{n\ell'm\sigma}(r)|^2 \int d^2\Omega Y_{\ell'm}^*(\theta, \phi) Y_{\ell'm}(\theta, \phi) Y_{\ell 0}(\theta, \phi). \quad (25)$$

For a given effective potential, the energy is evaluated from

$$E = \int dr r^2 \sum_{n\ell m\sigma} \phi_{n\ell\sigma}^* [\hat{T}_\ell + V_{\text{EXT}}(r)] \phi_{n\ell\sigma} + E_{\text{HXC}} \quad (26)$$

where  $T_\ell = P_r^2/2m + l(l+1)/2mr^2$  and the sum is over occupied states only.

The gradient of the energy with respect to the effective potential is evaluated from the relevant special case of Eq. (17)

$$\frac{\partial E}{\partial V_{\sigma\text{HXC}}(r)} = - \sum_{nl\sigma} M_{nl\sigma} (g_{nl\sigma}^*(r)\phi_{nl\sigma}(r) + \phi_{nl\sigma}^*(r)g_{nl\sigma}(r)), \quad (27)$$

where  $g_{nl\sigma}(r)$  is the solution to a one-dimensional version of Eq. (18):

$$(H_l - e_{nl\sigma})g_{nl\sigma}(r) = \frac{1}{M_{nl\sigma}} \frac{\partial E_{\text{HXC}}}{\partial \phi_{nl\sigma}^*(r)} - (V_{\sigma\text{HXC}}(r) + \lambda_{nl\sigma}) \phi_{nl\sigma}(r), \quad (28)$$

$M_{nl\sigma}$  is the occupancy of the subshell with quantum numbers  $\{nl\sigma\}$ . We solved Eq. (28) numerically subject to the constraint Eq. (20).

We have implemented the foregoing for two choices of energy functionals. The first is a conventional local spin density approximation (LSDA) functional.<sup>11</sup> The second, the so-called exact-exchange (EEX) functional, evaluates the Hartree-Fock energy with Kohn-Sham orbitals. For this functional, there is no correlation contribution. All calculations were done with radial meshes adequate to converge the total energy to an accuracy of  $1 \times 10^{-6}$  Hartree (1 Hartree = 27.211396 eV).<sup>12</sup> For a representative set of atoms, He, Ca, Cr, Sr, Mo, Tc, Pd, and Pt, we find that our gradient search LSDA calculations converge to the same ground-state energy as the self-consistent LSDA calculations to within  $4 \times 10^{-7}$  Hartree. In addition, the exchange-correlation energy, which is not variational, agrees to within  $7 \times 10^{-6}$  Hartree in all cases. This agreement gives us confidence that our numerical mesh and convergence are quite accurate. Similarly, our gradient search EEX calculations are in good agreement with the results of Engel and Vosko,<sup>4</sup> as seen in Table I. The worst agreement is for Pt, where the difference in total energy is  $4 \times 10^{-4}$  Hartree. For all systems, the difference in exchange energy between the two calculations is the same (to within  $\pm 1 \times 10^{-4}$  Hartree) as the difference in total energy. Given the level of convergence we have demonstrated with the LSDA calculations, we suspect that the disagreement is due to different radial meshes. There are slightly larger differences with the calculations of Fritsche and Yuan.<sup>8</sup> These differences may be due to a different level of self-consistency, or the parameterization of the potential in those calculations. For the EEX calculations, there is an additional convergence test. In completely self-consistent EEX calculations, the virial theorem states that the kinetic energy is exactly equal to the negative of the total energy. In the present calculations, the kinetic energy differed from the negative of the total energy by less than  $5 \times 10^{-4}$  Hartree.

One drawback of this method is that it does not accurately treat the asymptotic (large  $r$ ) part of the potential. Since the total energy is not very sensitive to the asymptotic part of the potential, the gradient of the energy with respect to that part of the potential is quite small. Since the gradient is small, the asymptotic part of the potential does not get updated very quickly. The problem with

this insensitivity is compounded because this method is not sensitive to an overall shift of the potential. During minimization, the potential close to the core shifts up and down relative to the zero of the potential. Thus, the potential far from the nucleus is quite poorly behaved. Because the potential can shift relative to vacuum, the absolute values of the eigenvalues are ill-defined. On the other hand, eigenvalues differences agree well with fully self-consistent calculations. The poor convergence of the asymptotic part of the potential is in contrast to the work of Fritsche and Yuan.<sup>8</sup> In their approach the potential is parameterized in a way that forces it to have the correct asymptotic form. For our intended application, the electronic structure of solids, the poor convergence of the asymptotic potential will not be an issue.

To test the convergence of this method both in terms of accuracy and in terms of speed, we carried out additional tests using the LSDA functional. In Figure 1, we show the convergence of the total energy as a function of the number of evaluations of the atomic energy. The figure compares the convergence properties of a typical self-consistent mixing scheme<sup>13</sup> and a gradient search implemented using a quasi-Newton method.<sup>14</sup> As expected for a situation where the output potential is easy to calculate, the mixing scheme is much faster. On the other hand, for functionals where the output potential is time-consuming to compute compared to the gradient (such as the integral equation method), a gradient search can achieve good accuracy with a reasonable number of gradient evaluations.

Also shown in Figure 1 is the convergence of the exchange-correlation energy (dotted lines). Since only the total energy is variational, the convergence of any of its parts is much slower, and non-monotonic. For any convergence scheme, converging individual contributions to the total energy to a given accuracy requires more iterations than converging the total energy to that accuracy.

The calculations shown in Figure 1 used a modified Thomas-Fermi potential as a starting approximation. In Figure 2, we show that starting with a better approximation leads to faster convergence. The results in Figure 2 are for the exact-exchange functional using the fully self-consistent LSDA potential as a starting approxima-

tion. The difference between the initial energy and the converged result is more than two orders of magnitude smaller than starting with the modified Thomas Fermi potential used to generate the results in Figure 1.

With the quasi-Newton method, it is possible to vary the number of previous iterations that are kept. Figure 2 shows how the convergence varies as this number is varied. In the limit that only the previous iteration is saved, the results are comparable to the results of a conjugate-gradient minimization (dotted line). The conjugate-gradient results could be significantly improved with use of a better preconditioner. Unfortunately, we were not able to find a better one. It may be that there is no good *diagonal* approximation to the Hessian. In that case the advantage of constructing a non-diagonal approximation as is done in the quasi-Newton method is clear. Figure 2 shows that at least for this system, it is possible to find the total energy to an accuracy of  $1 \times 10^{-3}$  eV with about 10 iterations using about 15 calculations of the gradient.

Ultimately, we are interested in using this method to study crystalline magnetic systems. To check how well the EEX functional reproduces magnetic effects, we calculated the energy of several single-determinant multiplets for the Ti atom. Table I compares our results with the corresponding energies obtained from a Hartree-Fock calculation. The agreement is surprisingly good considering that the Hartree-Fock calculations use orbital-dependent, non-local potentials and the exact-exchange Kohn-Sham calculations use a single, orbital-independent, local, and spherical effective potential. Since the  $3d$ -level is partially filled in all multiplets we have considered, the atomic density is non-spherical. While it is known that the EEX gives ground state energies for atoms that are close to those found by Hartree-Fock, we are unaware of any such test of excited states for non-spherical atoms. This agreement gives us hope that functionals based on EEX (with appropriate correlation functionals) will properly describe the exchange interactions that in atoms give rise to Hund's second rule for partially filled levels. The exclusion of these interactions from LSDA is thought to be responsible for some of the inaccuracies in the description of magnetic systems.<sup>15</sup>

## V. SUMMARY

In this paper, we described a new method for use in electronic structure calculations where the energy functionals of interest are expressed explicitly in terms of Kohn-Sham orbitals. The method uses an effective scalar potential  $V_{\text{HXC}}(\mathbf{r})$  and an effective vector poten-

tial  $\mathbf{A}_{\text{HXC}}(\mathbf{r})$  as the independent variables in a gradient search algorithm to find the minimum of  $E$ . We demonstrated the method for atoms with spherical effective potentials using a local spin-density functional and an exact exchange functional. The results were encouraging and suggest that further development of the method is warranted.

## VI. ACKNOWLEDGMENTS

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	$E_{\text{tot}}$			$E_x$		
	Present	Reference 4	Reference 8	Present	Reference 4	Reference 8
He	-2.8617	-2.8617		-1.0258	-1.0258	
Ca	-676.7519	-676.7520	-676.7519	-35.1990	-35.1991	-35.2018
Cr	-1043.3457	-1043.3458		-47.7554	-47.7555	
Sr	-3131.5334	-3131.5336	-3131.5330	-101.9262	-101.9264	-101.9223
Mo	-3975.5371	-3975.5373		-119.8941	-119.8943	
Tc	-4204.7793	-4204.7795		-124.3767	-124.3769	
Pd	-4937.9060	-4937.9062		-139.1135	-139.1136	
Pt	-17331.0931	-17331.0935		-331.3387	-331.3390	

TABLE I. Comparison of EEX calculations. All energies are in Hartrees (1 Hartree = 27.211396 eV).

Configuration	HF	EEX	Difference
$3d^2 4s^2 {}^3F(M=3)$	-848.4059	-848.3974	0.0085
$3d^2 4s^2 {}^3F(M=2)$	-848.4059	-848.3974	0.0085
$3d^2 4s^2 {}^1G$	-848.3321	-848.3227	0.0094
$3d^3 4s^1 {}^5F$	-848.3863	-848.3758	0.0105

TABLE II. Single determinant multiplet energies for Ti. All energies are in Hartrees (1 Hartree = 27.211396 eV), HF are Hartree-Fock calculations<sup>16</sup> and EEX are Kohn-Sham calculations using an “exact-exchange” formalism with a spherical effective potential.

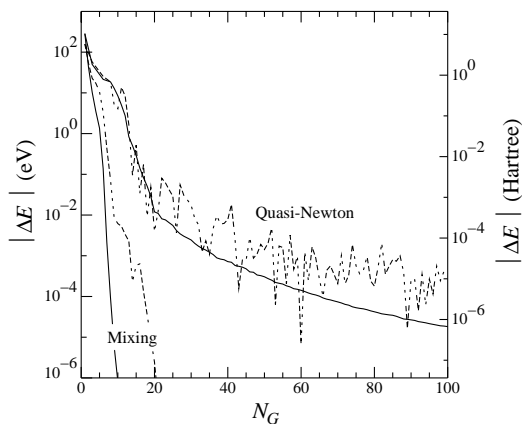


FIG. 1. Convergence of total energy calculations. For spin-polarized, spherical atomic Cr using the LSDA, the solid curves give the difference between the total energy and the fully self-consistent total energy and the dotted curves give the absolute value of the difference between the exchange-correlation energy and the fully self-consistent exchange-correlation energy as a function of number of energy computations,  $N_G$ . Two convergence schemes are considered, a method based on “mixing” input and output potentials and a gradient based, “quasi-Newton” method. Since the exchange-correlation energy is not variational, it varies between being greater than and less than the fully self-consistent result.

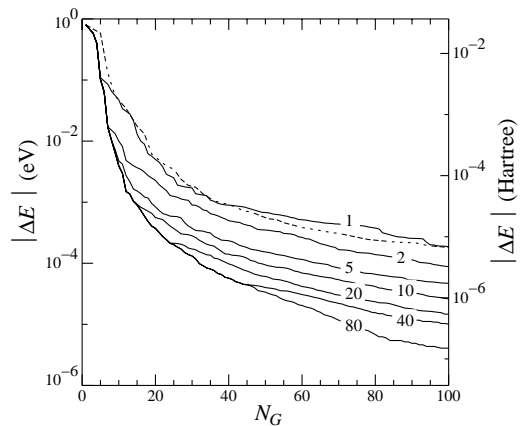


FIG. 2. Convergence of total energy calculations. For spin-polarized, spherical atomic Cr using the exact-exchange formalism, all curves give the difference between the total energy and the fully converged total energy as a function of number of energy computations,  $N_G$ . The solid curves show results for a quasi-Newton method, and are labeled by the number of previous iterations stored. The dotted curve shows results for a conjugate gradient method.