

Method for calculating wave functions in a nonspherical potential

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A new method is described for the solution of the single-particle Schrödinger equation in which the potential is nonspherical. This method is more efficient than methods based on spherical-harmonic expansions, both in terms of computer time and storage. The method is distinguished by the use of a "ray" representation in which (a) the potential is diagonal, (b) the nondiagonal portion of the Laplacian is small, and (c) boundary conditions are easily imposed. Illustrative applications to the orbital and total energies of free atoms are described.

INTRODUCTION

The effective single-particle potential "seen" by the electrons in most atoms, and all solids, is nonspherical or angle dependent. In many methods of solving Schrödinger's equation [e.g., the central-field method¹ for atoms, or the muffin-tin augmented plane waves (APW) (Ref. 2) or Korringa-Kohn-Rostoker (KKR) (Ref. 3) methods for solids], this nonsphericity is ignored, and the potential is approximated by its spherical average. This leads to a great simplification of the calculations, and is believed to be a good approximation both for atoms and for close-packed solids.

There is, however, a class of interesting problems in which these nonspherical effects play an important role. This class includes quantities associated with the electron density near the nucleus, such as hyperfine fields, quadrupole moments, spin-resonance amplitudes, and Hellmann-Feynman forces, as well as quantities associated with the electron density farther from the nucleus, such as the contribution of the anisotropy of the valence d shell to the structural stability of transition metals. This entire class of problems is either impossible or very difficult to address using pseudopotential theory.⁴ Even approaches such as the linear-combination-of-atomic-orbitals (LCAO) method,⁵ which do not assume the atomic interior to be spherical, may not allow sufficient variational flexibility to describe the subtle electron-density rearrangements responsible, for example, for the nonspherical contributions to the total-energy difference between different structures. It is important to note in this context that calculational procedures for polyatomic systems that are based on augmentation, e.g., (APW) (Ref. 6) and augmented spherical waves (ASW),^{6,7} permit the detailed description of the atomic interior to be performed independently for each atom. The procedure presented here for the description of the atomic interior was developed in part for synthesis with APW- and ASW-like procedures.

METHOD

We consider here the solutions of a single-particle Schrödinger equation

$$[-\nabla^2 + V(\vec{r})]\psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}). \quad (1)$$

Equations of this type must be repeatedly solved, for example, in self-consistent-field descriptions of electronic structure. Many such calculations employ the density-functional⁸ description of exchange and correlation, in which case the single-particle potential $V(\vec{r})$ appearing in Eq. (1) is given by

$$V(\vec{r}) = V_{\text{nuc}}(\vec{r}) + \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + \mu_{\text{xc}}(\vec{r}). \quad (2)$$

Here $V_{\text{nuc}}(\vec{r})$ is the nuclear potential, and $\rho(\vec{r})$ is the electronic charge density, to be obtained self-consistently from the energetically lowest N solutions of Eq. (1),

$$\rho(\vec{r}) = \sum_{i=1}^N |\psi_i(\vec{r})|^2 \quad (3)$$

for an N -electron system.

The quantity $\mu_{\text{xc}}(\vec{r})$ is the exchange-correlation potential; it is a universal (system-independent) functional of the charge density.⁹ Its exact form is unfortunately unknown, but there is a considerable body of experience suggesting that the "local-density approximation", where μ_{xc} is approximated by its dependence on the charge density for the homogeneous electron gas, is adequate for many applications.¹⁰ While the method of solving Schrödinger's equation to be described does not depend explicitly on the use of this approximation, all the results discussed below were obtained using the local-density approximation.

The spherical approximations that have been used in the past for solving Eq. (1) consist of surrounding each nucleus in the system by a sphere, inside which the potential of Eq. (2) is replaced by its spherical average. (One thinks of an atom as being centered in a very large sphere

in this context.) We consider here the problem of a nucleus and electronic charge density embedded in a sphere within which the potential is nonspherical (for an atom, the nonsphericity arises from anisotropy in the charge density within the sphere; in solids, there are additional nonspherical terms arising from the charge density in other spheres, and from the charge density between spheres).

One approach to this nonspherical problem consists of expanding the potential and wave functions in spherical harmonics, obtaining a set of $(l_{\max} + 1)^2$ radial equations (one for each l and m).^{11,12} The angular part of the Laplacian is diagonal in this representation, but the potential is not, due to its nonsphericity, so that these radial equations are coupled.

Even the replacement of the $l_{\max} + 1$ uncoupled equations of the central-field model by the $(l_{\max} + 1)^2$ coupled equations for a general potential does not reveal the full magnitude of the problem. Additional complications enter when, for example, the solutions corresponding to the discrete part of the eigenenergy spectrum (the core states) are constructed, because the angular behavior of such solutions at large distances from the nucleus is not known. That is, not only does a particular solution of the coupled system of equations consist of $(l_{\max} + 1)^2$ functions of the radius; the desired wave function corresponding to a discrete eigenenergy is, in general, a linear combination of $(l_{\max} + 1)^2$ such particular solutions. (Each of these $(l_{\max} + 1)^2$ solutions corresponds to different boundary conditions on the surrounding sphere.) So, where in the central-field case a particular core state is constructed from a single function of the radius, the general case requires the construction of $(l_{\max} + 1)^4$ functions. The approach described here does not eliminate this information explosion, but it reduces the problem considerably.

A second disadvantage of the use of the angular-momentum representation in this context is the manner in which it describes the rapid radial variation of orbitals in the core region. The nonspherical potential causes small phase changes in the core oscillations; that is, the peaks and nodes of the wave function occur at slightly different radii in different directions. In the angular-momentum representation, which focuses on the direction dependence of the wave function at a *single* radius, a small phase change in a rapid radial variation is viewed as a rapid direction variation. Such rapid angular variations require high-order spherical harmonic expansions for their description. An l_{\max} of 4, for example, will adequately describe angular variations only on a scale of (roughly) $4\pi/25$ steradians, but will require the simultaneous

solution of 25 sets of 25 coupled radial equations.

An alternative method which avoids these difficulties can be constructed. In this method, the potential and wave functions are computed on an angular mesh of N_r "rays". (The directions of these rays can be chosen so as to exactly integrate spherical harmonics with angular momentum l less than some value l_{\max} .) In the ray representation, the potential is diagonal, but the angular part of the Laplacian is not. The ray representation is thus complementary to the spherical-harmonic representation, and one can think of these two representations as a transform pair. We generate a set of solutions $\chi_L(\vec{r}, \epsilon)$, where ϵ is the energy and $L \equiv (l, m)$ indicates the angular behavior of the solution near the origin:

$$\lim_{r \rightarrow 0} \chi_L(\vec{r}, \epsilon) = r^l Y_L(\hat{r}), \quad (4)$$

where $Y_L(\hat{r})$ is a spherical harmonic. For the construction of individual members in this set, we decompose the total Hamiltonian into two l -dependent terms:

$$H = -\nabla^2 + V(\vec{r}) = H_l^0 + \delta H_l, \quad (5)$$

where H_l^0 is diagonal in the ray representation:

$$H_l^0 = -\frac{1}{r} \frac{d^2}{dr^2} r + V(\vec{r}) + \frac{l(l+1)}{r^2} \quad (6)$$

and δH_l is the remainder of the Hamiltonian. The operator δH_l is not diagonal in the ray representation, but the usual spherical-harmonic representation of the angular-momentum operator L^2 ,

$$\langle \hat{r} | L^2 | \hat{r}' \rangle = \sum_{L'} Y_{L'}^*(\hat{r}) L'(L'+1) Y_{L'}(\hat{r}') \quad (7a)$$

$$= \frac{1}{4\pi} \sum_{L'} (2L'+1) L'(L'+1) P_{L'}(\hat{r} \cdot \hat{r}'), \quad (7b)$$

provides a straightforward, and computationally convenient, representation of δH_l :

$$\delta H_l = \frac{1}{r^2} [\langle \hat{r} | L^2 | \hat{r}' \rangle - l(l+1) \delta(\hat{r} - \hat{r}')]. \quad (8)$$

The function $P_l(\hat{r} \cdot \hat{r}')$ is a Legendre polynomial.

We first find solutions of H_l^0 (Eq. 6) along each ray, proceeding as if the rays were completely independent of one another. (The solutions along each ray can be constructed using standard methods for the spherical problem.) Letting the single index ν specify the principal quantum number n , as well as l and m , we construct a set of solutions $\chi_\nu(\vec{r}) = \chi_{nlm}(\vec{r}, \hat{r})$, each characterized by its angular behavior near the origin (Eq. 4) and possessing $n-1$ radial nodes along each ray. Such functions are not eigenfunctions of either H or H_l^0 , because a different energy, $\epsilon_\nu(\hat{r})$, is required along each

ray to satisfy the boundary conditions on the surrounding sphere. Nonetheless, the functions $\{\chi_\nu(\mathbf{r})\}$ constitute an excellent basis set with which to synthesize approximate eigensolutions. That is, we expand the desired solutions $\psi(\mathbf{r})$ as follows:

$$\psi(\mathbf{r}) = \sum_\nu c_\nu \chi_\nu(\mathbf{r}), \quad (9)$$

and determine the expansion coefficients c_ν by minimizing $\langle \psi | (H - \epsilon) | \psi \rangle$. The linear equations for the c_ν are

$$\sum_\nu \langle \nu | H - \epsilon | \nu' \rangle c_\nu = 0. \quad (10)$$

The normalization integrals $\langle \nu | \nu' \rangle$ are given by

$$\langle \nu | \nu' \rangle = \int d\hat{r} S_{\nu\nu'}(\hat{r}), \quad (11)$$

where

$$S_{\nu\nu'}(\hat{r}) = \int dr r^2 \chi_\nu(r, \hat{r}) \chi_{\nu'}(r, \hat{r}). \quad (12)$$

The matrix elements of H_l^0 (Eq. 6) in this basis involve a single sum over rays:

$$\langle \nu | H_l^0 | \nu' \rangle = \int d\hat{r} \epsilon_{\nu\nu'}(\hat{r}) S_{\nu\nu'}(\hat{r}). \quad (13)$$

The matrix elements of δH_l (Eq. 8) require a double sum over rays,

$$\langle \nu | \delta H_l | \nu' \rangle = \int dr \int d\hat{r} \int d\hat{r}' \chi_\nu(r, \hat{r}) \langle \hat{r} | L^2 | \hat{r}' \rangle \chi_{\nu'}(r, \hat{r}') - l(l+1) \int dr \int d\hat{r} \chi_\nu(r, \hat{r}) \chi_{\nu'}(r, \hat{r}), \quad (14)$$

where $\langle \hat{r} | L^2 | \hat{r}' \rangle$ is given by Eq. (7).

This procedure, of initially setting up a basis set as though the rays were independent, has a number of attractive features: The zero-value boundary condition for core states on the surrounding sphere is easily implemented [the angular behavior of the wave function at large r is completely determined by continuity and the condition that Eq. (4) is satisfied on all rays], and root-finding and wave-function construction, a substantial part of the overall calculation are performed before the coupling between rays induced by δH_l is introduced, leading to a considerable savings in computation time (as long as the rays are uncoupled, the computation time is proportional to N_r rather than N_r^2).

In practice, more time is spent in constructing $\langle \nu | \delta H_l | \nu' \rangle$ than is spent in setting up the basis functions $\chi_\nu(r, \hat{r})$, so that the iteration to a self-consistent solution of Eq. (1) can be speeded up considerably if a way is found to minimize the number of times this quantity must be computed. One approximation which suggests itself is to iterate to self-consistency neglecting δH_l , and then, once a self-consistent potential has been found, to repeat the calculation including the effects of δH_l . In this way, approximate self-consistency is achieved in a time proportional to N_r . It is a remarkable fact that in all the calculations we have performed, inclusion of δH_l after achieving approximate self-consistency has very little effect.

RESULTS

Our method has been applied to ground-state calculations for a number of atoms, and we now describe the results of these calculations. The an-

gular mesh used is described in Ref. 13; this mesh has $N_r = 42$, and is capable of exactly integrating spherical harmonics with $l \leq 8$. (For atoms with d electrons, the charge density will have components with $l = 4$, and quantities entering the total energy, such as the charge density times the electrostatic potential, will have components with $l = 8$.)

The results of the calculations for several atoms are given in Table I. In this table, the total energies for both spherical and the full nonspherical calculations are given for boron (both spin-polarized and unpolarized), for the p_x^2 configuration of carbon (spin unpolarized), for the $p_x p_y$ configuration of carbon (both spin-polarized and unpolarized), for the $d^6 s$ configuration of manganese (spin-polarized only), for the $d^6 s^2$ and $d^7 s$ ($d_{x^2-y^2} d_{3z^2-2}$) configurations of iron (both spin-polarized and unpolarized), and for the $d^9 s^2$ configuration of copper (spin-polarized only). The quantity ΔE in this table is the nonspherical total energy minus the spherical total energy; the remaining quantities in Table I are discussed below.

Perhaps the most interesting feature of these results is that taking full account of the nonsphericity *raises* the total energy of most atoms, whereas one expects the true ground state to be nonspherical, so that the total energy should decrease. This nonintuitive result is an artifact of the so-called self-interaction associated with the local-density approximation. Consider, for example, the carbon atom. The (spherical) central-field model implicitly puts $\frac{2}{3}$ of an electron in each $2p$ orbital (this makes the p orbitals degenerate, so that a self-consistent charge density exists). In the p_x^2 configuration, on the other hand, the Coulomb self-interaction will be larger than in

TABLE I. Total atomic energies (Ry) for spherical and nonspherical calculations (*NP*=non-spin-polarized; *P*=spin-polarized). ΔE is the nonspherical-spherical energy difference, ΔE_p is the first-order perturbation-theory estimate of this energy difference, and ΔU and ΔE_{xc} are the Coulomb and exchange-correlation contributions to ΔE_p (see text).

	Spherical	Nonspherical	ΔE	ΔE_p	ΔU	ΔE_{xc}
B (<i>NP</i>)	-48.705	-48.698	+0.007	+0.007	0.029	-0.022
B (<i>P</i>)	-48.726	-48.729	-0.003	-0.004	0.030	-0.034
C p_x^2 (<i>NP</i>)	-74.869	-74.812	+0.057	+0.054	0.147	-0.093
C $p_x p_y$ (<i>NP</i>)	-74.869	-74.857	+0.012	+0.012	0.037	-0.025
C $p_x p_y$ (<i>P</i>)	-74.962	-74.960	+0.002	+0.001	0.038	-0.037
Mn $d^6 s$ (<i>P</i>)	-2297.139	-2297.137	+0.002	-0.003	0.037	-0.040
Fe $d^6 s^2$ (<i>NP</i>)	-2522.092	-2522.059	+0.033	+0.028	0.049	-0.021
Fe $d^6 s^2$ (<i>P</i>)	-2522.355	-2522.347	+0.008	+0.003	0.046	-0.043
Fe $d^7 s$ (<i>NP</i>)	-2522.174	-2522.163	+0.011	+0.011	0.039	-0.028
Fe $d^7 s$ (<i>P</i>)	-2522.347	-2522.361	-0.014	-0.018	0.037	-0.055
Cu $d^9 s^2$ (<i>P</i>)	-3275.279	-3275.260	+0.019	+0.010	0.058	-0.048

the spherical case, because, when only the p_x orbital is occupied, the charge density is more localized in angle (it has the form of a single p lobe, rather than being the spherical average of three spatially orthogonal p lobes). In an exact treatment of exchange and correlation, this increase in the Coulomb self-interaction is more than compensated by the effects of exchange and correlation,¹⁴ leading to a lowering of the total energy. In local-density theory, on the other hand, this cancellation is incomplete, because of the approximate treatment of exchange and correlation.

The inclusion of spin-polarization effects can be regarded as an improvement in the exchange-correlation approximation, and the fact (apparent in Table I) that inclusion of spin-polarization effects reduces the value of ΔE in every case is further evidence that a sufficiently accurate approximation for exchange and correlation would lead to negative values of ΔE for all atoms. In fact, the local-density approximation used in these calculations is occasionally good enough to give negative ΔE 's, as for B and Fe d^7 s, but this is clearly accidental.

The contribution of the self-interaction to the total-energy difference between spherical and nonspherical atoms is exhibited in detail by the variation of the orbital eigenenergies with occupation. The relevance of the orbital eigenvalues in this context is that they are the derivatives of the total energy with respect to occupation,¹⁵ and also that the difference between spherical and nonspherical atoms is simply a matter of occupation. In Fig. 1, for example, we show the $2p_z$ and $2p_x$

eigenvalues of spin-polarized carbon for the configuration $2p_x^{2/3+n} 2p_y^{2/3+n} 2p_z^{2/3-2n}$ as n varies between zero and $\frac{1}{3}$. For $n=0$, this is the spherically-averaged p^2 configuration, and for $n=\frac{1}{3}$, it is the fully nonspherical $p_x p_y$ configuration. The figure thus shows how the $2p$ eigenvalues change as the charge density is changed in a continuous way from spherically averaged to fully nonspherical. Note that the spherically-averaged configuration is itself an example of fractional occupation, $\frac{2}{3}$ of

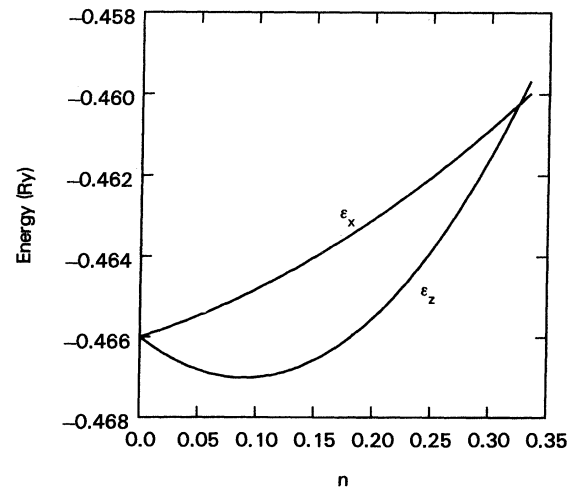


FIG. 1. Eigenvalues ϵ_x and ϵ_z of the p_x and p_z states of spin-polarized C in the configuration $2p_x^{2/3+n} 2p_y^{2/3+n} 2p_z^{2/3-2n}$. A spherically-averaged charge density corresponds to $n=0$, and $n=\frac{1}{3}$ corresponds to the nonspherical configuration $p_x p_y$.

an electron in each of the three p orbitals. Note also that as the occupation of p_x and p_y is increased, their eigenvalues rise, and as the occupation of p_z is decreased, its eigenvalue first falls and then rises (for the same reasons as outlined above¹⁴). For most values of n in this figure, the assumed configuration is not a ground-state configuration, because the atom has unoccupied states below the highest occupied state. However, at both end points ($n=0$ and $n=\frac{1}{3}$), a self-consistent ground-state charge density exists, because at $n=0$ the degeneracy of the p levels is consistent with fractional occupation. The p_z level crosses the p_x and p_y levels for n slightly less than $\frac{1}{3}$, and there are no holes below the highest occupied state to the right of this crossover point. The occurrence of this crossover is an accidental consequence of the exchange-correlation approximation, and does not occur in most other atoms. In fact, of all the calculations given in Table I, only spin-polarized B and spin-polarized C $p_x p_y$ are true ground-state calculations; all the others have either fractional occupations or unoccupied levels below the highest occupied level (the spherically symmetric Mn $d^5 s^2$ and Cu $d^{10} s$ configurations, not presented in Table I, are the ground-state configurations of these atoms).

Another important result of these calculations is that it appears to be adequate, for purposes of estimating the total-energy difference between spherical and nonspherical atoms, to treat the nonspherical contributions by the use of perturbation theory. Suppose that one forms an approximate nonspherical charge density by taking the radial wave functions from a *self-consistent* spherically-averaged calculation and multiplying by the appropriate spherical harmonics. The total energy corresponding to this approximate charge density can be found as follows: There will be no change in either the kinetic energy, or in the electrostatic interaction energy between the electrons and the nucleus, compared to the spherically-averaged calculation. The only changes will be in the electron-electron interaction energy and in the exchange-correlation energy. Denoting these energy changes by ΔU and ΔE_{xc} , respectively, we find a perturbation-theory estimate of the change in the total energy, ΔE_p , given by

$$\Delta E_p = \Delta U + \Delta E_{xc}. \quad (15)$$

The three quantities ΔE_p , ΔU , and ΔE_{xc} are all given in Table I, where it is seen that ΔE_p is remarkably close to ΔE , especially for the lighter atoms (values for ΔU and ΔE_{xc} for C are in perfect agreement with those obtained earlier by von Barth¹⁶). This is a rather striking illustration of the variational nature of the total energy, in the

sense that both ΔU and ΔE_{xc} are very different from the changes in the electron-electron interaction energies and exchange-correlation energies that are found from the self-consistent nonspherical results. That is, both ΔU and ΔE_{xc} are poor estimates of the true values of these changes, but their sum is a good estimate of the change in total energy.

A further indication of the usefulness of perturbation calculations is given in Table II, where we show the configurational-energy differences $E(d^{n+1}s) - E(d^n s^2)$ for several transition-metal atoms. In this table, we compare values for this energy difference as obtained from spherically averaged calculations, from the full nonspherical calculations, from perturbation-theory estimates of the nonspherical corrections to the total energy, and, for purposes of comparison, the perturbation-theory results obtained earlier by Gunnarsson and Jones.¹⁷ It is seen that the perturbation calculations give an adequate representation of total-energy changes, as well as total energies themselves. Since such perturbation calculations avoid the time-consuming iteration to self-consistency of the full nonspherical Hamiltonian, this represents a useful simplification of atomic total-energy calculations.

Finally, we show in Table III the effects of neglecting δH_i for a non-spin-polarized calculation for Fe. The calculation was first iterated to self-consistency neglecting δH_i , and then was reiterated to self-consistency including the effects of δH_i . The table shows the $3d$ and $4s$ eigenvalues, the total energy, the negative of the total kinetic energy (which, by the virial theorem, should equal the total energy), and the electron-electron interaction energy (which is sensitive to small changes in the charge density) for four cases: (1) when

TABLE II. Configurational energy differences $E(d^{n+1}s) - E(d^n s^2)$ (Ry) for a number of transition-metal atoms (all calculations include the effects of spin polarization). First column (SP): configurational energy difference using spherically-averaged charge densities; second column (NS): configurational energy difference using the full nonspherical calculation; third column (PT): configurational energy difference obtained through the use of perturbation theory for the nonspherical corrections; fourth column (GJ): perturbation-theory results of Gunnarsson and Jones (Ref. 17). Full nonspherical calculations were not performed for Co and Ni.

	SP	NS	PT	GJ
Mn	0.071	0.073	0.068	0.08
Fe	0.008	-0.014	-0.013	-0.01
Co	-0.055		-0.070	-0.06
Ni	-0.117		-0.087	-0.10
Cu	-0.179	-0.198	-0.189	-0.20

TABLE III. Effect of δH_l on selected eigenvalues, total energy, total kinetic energy, and Coulomb self-energy of non-spin-polarized Fe (d^6s^2) (energies in Ry).

	Spherical self- consistent	δH_l off self- consistent	δH_l on first iteration	δH_l on self- consistent
ϵ_{4s}	-0.4029	-0.4022	-0.4026	-0.4029
ϵ_{3d}	-0.5948	-0.5438	-0.5435	-0.5444
E_{tot}	-2522.092	-2522.062	-2522.060	-2522.059
$-T$	-2522.092	-2522.059	-2522.033	-2522.061
$2U$	2140.777	2140.545	2140.545	2140.488

self-consistency has been achieved in the spherical approximation; (2) when self-consistency has been achieved neglecting δH_l ; (3) for the first (i.e., non-self-consistent) iteration when δH_l is included; and (4) when self-consistency has been achieved in the presence of δH_l . We identify differences between the self-consistent results obtained neglecting δH_l and those corresponding to the first iteration including δH_l with a perturbation-theory estimate of the importance of δH_l . We note that, as we expect, the inclusion of δH_l has significantly greater effect on the nonvariational form ($-T$) of the total energy. We note also that, when the computer programs responsible for the results shown in Table III are applied to a spherically symmetric problem, the amount by which the virial theorem is not satisfied ($E_{\text{tot}} + T$) is smaller by about an order of magnitude. We therefore interpret the value of 0.002 Ry for $E_{\text{tot}} + T$ shown in Table III as a measure of the impor-

tance of the only approximation made in our procedure, the finiteness of the basis set of χ_ν 's we use to diagonalize the full Hamiltonian (Eq. 10). We emphasize that the differences between the second and third columns of Table III are not a measure of the importance of nonspherical effects. The contribution of nonspherical effects to the total energy for the system considered in Table III is seen to be about 15 times as large as the contribution due to δH_l .

In summary, we have described a calculational procedure for solving the single-particle Schrödinger equation when the potential is nonspherical. There are two distinct aspects of our results. The first is that our procedure appears to provide an adequately accurate description of intra-atomic contributions to the total energy, hyperfine fields, etc., while reducing both the number of computations and the storage required with respect to procedures based on spherical-harmonic expansions. The other aspect of this work to which we call attention is the unexpected discovery of the relative unimportance of the angular-momentum operator in coupling the solutions along different rays extending from the nucleus. This unimportance should be useful in calculations in which the volume in which Schrodinger's equation must be solved is not a sphere. For example, in the description of molecules, some rays extend from an atomic nucleus to infinity, while others terminate in bond regions. Knowledge that the coupling among such rays could be safely neglected would have significant practical benefits.

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