

## Symmetry of the atomic electron density in Hartree, Hartree-Fock, and density-functional theories

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The density of an atom in a state of well-defined total angular momentum has a specific finite spherical harmonic content, without and with interactions. *Approximate* single-particle schemes, such as the Hartree, Hartree-Fock, and local density approximations, generally violate this feature. We analyze, by means of perturbation theory, the degree of this violation and argue that it is small. The correct symmetry of the density can be assured by a constrained-search formulation without significantly altering the calculated energies. We compare our procedure to the (different) common practice of spherically averaging the self-consistent potential. Kohn-Sham density functional theory with the *exact* exchange-correlation potential has the correct finite spherical harmonic content in its density; but the corresponding exact single-particle potential and wave functions contain an infinite number of spherical harmonics.

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## I. INTRODUCTION

Single-particle descriptions of electronic states and densities in atoms date back to their earliest models. Most of them involve the motion of individual electrons in some effective potential due to the nucleus and the other electrons; Bohr's early analysis of some atomic spectra involved this idea [1]. With the advent of wave mechanics, the idea took on the form of solving single-particle Schrödinger equations with this effective potential. Prominent examples are the Hartree and Hartree-Fock (HF) approximations [2–4], and density-functional theory (DFT) [5]. Of these, only DFT provides in principle an exact description of electron densities with their proper truncated spherical harmonic content. In practice, one is forced to adopt an approximate form for the exchange-correlation potential, such as the local density approximation (LDA). In carrying out such calculations, one computes the electronic states and effective potential iteratively, yielding a self-consistent potential and density.

The spherical symmetry of the nuclear potential yields states of well-defined angular momentum. However, except for  $S$  states, the resulting electron densities are generally *not* spherically symmetric. ( $S$  states and their spherical densities present no problem and will not be further considered.) As we shall see below, in states of well-defined angular momentum quantum numbers  $L$  and  $L_z$ , the exact density  $n(\vec{r})$  may be decomposed in the *finite* series

$$n(\vec{r}) = \sum_{l=0}^L n_{2l}(r) Y_{2l}^0(\vec{\Omega}), \quad (1)$$

where the  $n_{2l}(r)$  are radial functions and  $Y_{2l}^0(\vec{\Omega})$  are spherical harmonics.

The self-consistent densities obtained via the approximation schemes described above do not have this form. This form *can* be and often is obtained by introduction of a further approximation that, however, violates the minimum principle: the effective potential may be spherically averaged,

yielding single-particle states with good angular momentum quantum numbers and a resulting density of the form in Eq. (1). Such spherical averaging is of practical utility as it greatly reduces the numerical effort involved in carrying out the approximation schemes [6]. Nevertheless, the Hartree, HF, and LDA may all be expressed in terms of variational principles, implying that the use of spherical averaging leads to an overestimation of atomic energy levels. To our knowledge, the quantitative effect of this has only been checked in a small number of cases [7,8]. The effect is thought to be small since the resulting energies for many atoms are in quite good agreement with experiment [9].

In this paper, we will examine this, to our knowledge largely unexplored, issue in some detail. Using a perturbative approach, we will demonstrate that the inappropriate spherical harmonic components appearing in the self-consistent density (without spherical averaging) are generally quite small. (An *exact* DFT calculation would, of course, yield the exact density with the correct spherical harmonic content.) We then develop a constrained search principle to modify the variational principles involved in the Hartree, HF, and DFT approximations to guarantee that the resulting density has the correct form of Eq. (1). We show in the context of the Hartree approximation that this approach generates energies that are only slightly higher than those from the unconstrained approximation.

It is interesting to consider in more detail the implications of Eq. (1) for *exact* DFT. Being exact [5], it is unnecessary to introduce constraints to guarantee this ‘‘symmetry’’ of the density. What is the angular symmetry of the exact effective single-particle potential entering the Kohn-Sham equations that guarantees that the density will have this form? A natural but incorrect guess would be that the Hartree and exchange-correlation potentials together sum to a potential that is spherically symmetric. In fact this is generally not true: the effective single-particle potential contains spherical harmonic components of *all* even orders. (A concrete example of this is presented in Appendix A.) Indeed, it has been shown [10,11] that a unique, spherically symmetric

single-particle potential  $v_0(r)$  may be chosen to match the spherical component  $n_0(r)$  of the density; it is possible to formulate an alternative to the Hohenberg-Kohn theorem based solely on  $n_0(r)$  [10]. However, the resulting potential yields incorrect higher-order components of the density  $n_{2l}(r)$  ( $l > 0$ ). Thus, there is a kind of complementarity: if one insists that the density has the correct truncated spherical harmonic content for an interacting state of well-defined angular momentum, the effective single-particle potential will not have spherical symmetry and the single determinant model wave function will *not* have good angular momentum quantum numbers. By contrast, if one insists that the single-particle potential be spherically symmetric, the correct spherical harmonic content of the density of the interacting state cannot be reproduced.

The remainder of this paper is organized as follows. In Sec. II, we first give the proof of Eq. (1). By a perturbative approach to the Hartree approximation, we demonstrate that the deviation of the density from its appropriate symmetry is actually quite small in a specific example (a helium triplet state), and comment on related results for the HF approximation and LDA. In Sec. III, we formulate a constrained-search approach to single-particle approximations for the density, which we apply to the Hartree approximation and the LDA. We summarize our results in Sec. IV. Finally, two appendixes are included. In Appendix A, we discuss a two-electron harmonic atom with interactions and show explicitly that the density of its lowest triplet state cannot be reproduced by a noninteracting system in a spherically symmetric effective single-particle potential. Appendix B contains some details of the numerical calculations.

## II. SPHERICAL HARMONIC CONTENT OF THE DENSITY

### A. Finite spherical harmonic content of the density

We begin by proving Eq. (1) of the Introduction by a standard application of the Wigner-Eckart theorem. Consider an atom in a state  $|L, M\rangle$  with total orbital angular momentum  $L$  and total azimuthal angular momentum  $L_z = M$  along the  $z$  direction. We ignore spin-orbit coupling, so that the orbital and spin states of the atom may be specified separately. We are interested in the expectation value of the operator  $n(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i)$ , where  $\vec{r}_i$  denotes the position of the  $i$ th electron. A useful decomposition of the delta function in this context is [12]

$$\delta(\vec{r} - \vec{r}_i) = \frac{1}{r^2} \delta(r - r_i) \sum_{l=0}^{\infty} \sum_{m=-l}^l Y_l^{-m}(\vec{\Omega}) Y_l^m(\vec{\Omega}_i),$$

where  $\vec{\Omega}$  represents an angular direction in spherical coordinates. The set  $\{Y_l^m(\vec{\Omega}_i), m = -l, -l+1, \dots, l\}$  constitutes an irreducible tensor operator with respect to the angular momentum operator  $L$ , and obeys the Wigner-Eckart theorem [13]. It follows that  $\langle L, M | Y_l^m(\vec{\Omega}_i) | L, M \rangle$  is proportional to the Clebsch-Gordon coefficient  $\langle LIMm | LIMm \rangle$ , which vanishes unless  $m = 0$ ,  $0 \leq l \leq 2L$ , and  $l$  is even. Substituting

the expansion for the delta function into the expectation value of the density and using the above observation directly yields Eq. (1).

### B. Infinite spherical harmonic content in the Hartree and Hartree-Fock approximations

The decomposition of the physical density of an atomic state in spherical harmonics consists of a finite series. However, the Hartree, HF, and approximate DFT solutions do *not* produce densities with this property. For example, suppose we *could* find a finite decomposition for the density in the Hartree approximation,

$$n^H(\vec{r}) = \sum_{l=0}^{l_{max}} \sum_{(l \text{ even})} n_l(r) Y_l^0(\vec{\Omega}).$$

The effective single-particle potential contains a term of the form

$$\lambda e^2 \int d^3 r' \frac{n^H(\vec{r}')}{|\vec{r} - \vec{r}'|},$$

where  $\lambda$  ( $0 \leq \lambda \leq 1$ ) is a parameter by which we may switch on the electron-electron interaction, which will be useful below. This term has a spherical harmonic decomposition with maximum  $l = l_{max}$ . The effective potential in the single-particle Schrödinger equation multiplies a wave function  $\phi$ ; for a single-particle state of azimuthal quantum number  $m = 0$  this may be expanded as

$$\phi(\vec{r}) = \sum_{l'=0}^{l'_{max}} y_{l'}(r) Y_{l'}^0(\vec{\Omega}). \quad (2)$$

When multiplied by the potential, the resulting products of spherical harmonics may be expressed as linear combinations of single spherical harmonics  $Y_l^0$ , with a maximum nonvanishing contribution from  $l = l_{max} + l'_{max}$ . The other terms in the Schrödinger equation, however, contain spherical harmonics of order  $l$  no greater than  $l'_{max}$ . Thus, the Schrödinger equation *cannot* be solved by wave functions expressible in a finite spherical harmonic expansion (except for the trivial case of  $L' = 0$ ).

The density produced from these wave functions in general has no finite spherical harmonic expansion. One way to demonstrate this uses perturbation theory. The solution to the Hartree equations may be expressed as a power series in  $\lambda$ ; terms of higher order involve increasingly larger orders of spherical harmonics. When reorganized as a spherical harmonic expansion, all orders will occur with each coefficient being a power series in  $\lambda$ . It is not possible for these coefficients to vanish for arbitrary values of  $\lambda$ .

As a concrete example, we analyze a two-electron atom in a triplet spin state with total angular momentum  $L = 1$ , whose density is not spherically symmetric. Using perturbation theory in the electron-electron interaction, we compute the density in the Hartree approximation. The Hamiltonian for our system is

$$H = \sum_{i=1,2} \left[ -\frac{1}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} \right] + \lambda e^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|}, \quad (3)$$

where  $Z$  is the nuclear charge. The fully interacting system is given by  $\lambda=1$ , and we will formally develop our perturbation theory in powers of  $\lambda$ . Alternatively, one may set  $\lambda=1$  and consider an expansion of energy and density in powers of  $1/Z$ , which is equivalent to an expansion in  $\lambda$ . Physically, one should thus think of the small  $\lambda$  limit as the state of a highly ionized atom of large  $Z$ . The specific case we will focus on is  $N=2$ ; thus  $\lambda=1$  and  $Z=2$  describes the helium atom.

In the absence of interactions, the state of interest to us involves one electron in a  $1s$  state and one in a  $2p$  state that we take to be in the  $m=0$  state. It is easy to see that the density of this state satisfies Eq. (1):

$$\begin{aligned} n^{(0)}(\vec{r}) &= |\phi_0^{(0)}(\vec{r})|^2 + |\phi_1^{(0)}(\vec{r})|^2 \\ &= |R_{10}(r)Y_0^0(\vec{\Omega})|^2 + |R_{21}(r)Y_1^0(\vec{\Omega})|^2 \\ &= [c_{00}^0 R_{10}(r)^2 + c_{11}^0 R_{21}(r)^2] Y_0^0(\vec{\Omega}) \\ &\quad + c_{11}^2 R_{21}(r) Y_2^0(\vec{\Omega}). \end{aligned} \quad (4)$$

In Eq. (4),  $\phi_0^{(0)}$  and  $\phi_1^{(0)}$  are, respectively, the  $1s$  and  $2p$  states,  $R_{nl}(r)$  are hydrogenic radial functions, with  $n$  the principal quantum number and  $l$  the angular momentum; the coefficients  $c_{jk}^i$  are defined as

$$c_{jk}^i = \int d\vec{\Omega} Y_i^0(\vec{\Omega}) Y_j^0(\vec{\Omega}) Y_k^0(\vec{\Omega}),$$

so that  $Y_j^0(\vec{\Omega}) Y_k^0(\vec{\Omega}) \equiv \sum_i c_{jk}^i Y_i^0(\vec{\Omega})$ . The coefficients  $c_{jk}^i$  are closely related to Gaunt coefficients commonly used in atomic structure calculations [9], and have properties similar to Clebsch-Gordon coefficients; in particular,  $c_{jk}^i = 0$  unless  $i+j+k$  is even and  $|j-k| \leq i \leq |j+k|$ . It is these two properties that guarantee the density of the noninteracting state has the truncated form in Eq. (1). The superscript (0) in Eq. (4) denotes noninteracting quantities ( $\lambda=0$ ).

The Hartree approximation amounts to self-consistently finding two single-particle eigenstates  $\phi_0$  and  $\phi_1$ , of energies  $\varepsilon_0, \varepsilon_1$ , for noninteracting electrons moving in an effective potential

$$V_{eff}^H = -\frac{Ze^2}{r_i} + \lambda e^2 \int d^3 r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}, \quad (5)$$

where the density is  $n(\vec{r}) = |\phi_0(\vec{r})|^2 + |\phi_1(\vec{r})|^2$ . To first order in perturbation theory, we may write that potential as

$$\begin{aligned} V_{eff}^H &= -\frac{Ze^2}{r_i} + \lambda e^2 \int d^3 r' \frac{n^{(0)}(\vec{r}')}{|\vec{r} - \vec{r}'|} + O(\lambda^2) \\ &\equiv -\frac{Ze^2}{r_i} + \lambda U^{(1)}(\vec{r}) + O(\lambda^2). \end{aligned}$$

The Schrödinger equation arising in the Hartree approximation may be solved within perturbation theory by expanding the effective potential, eigenstates, and eigenenergies in powers of  $\lambda$ . The first-order correction to the eigenstates satisfies the inhomogeneous differential equation

$$[H_0 - \varepsilon_i^{(0)}] \phi_i^{(1)}(\vec{r}) = [\varepsilon_i^{(1)} - U^{(1)}] \phi_i^{(0)}(\vec{r}), \quad (6)$$

where  $i=0,1$ , and the first-order correction to the energies are  $\varepsilon_i^{(1)} = \int d^3 r \phi_i^{(0)*}(\vec{r}) U^{(1)}(\vec{r}) \phi_i^{(0)}(\vec{r})$ . Because the density  $n^{(0)}(\vec{r})$  contains only even spherical harmonics, so will the potential  $U^{(1)}$ . It immediately follows that the wave function corrections  $\phi_i^{(1)}$  will have the same parity as the states  $\phi_i^{(0)}$  from which they descend. Using the multiplicative properties of the  $Y_l^0$  gives

$$\begin{aligned} \phi_0^{(1)} &= y_0(r) Y_0^0(\vec{\Omega}) + y_2(r) Y_2^0(\vec{\Omega}), \\ \phi_1^{(1)} &= y_1(r) Y_1^0(\vec{\Omega}) + y_3(r) Y_3^0(\vec{\Omega}), \end{aligned} \quad (7)$$

where  $y_i(r)$  are purely radial functions.

Our development of the perturbation theory already illustrates one of the central points of this paper: We can see that the effective potential (which we have computed to first order in  $\lambda$ ) is not spherically symmetric and the wave functions arising in the Hartree equation do not have well-defined angular momentum. By expanding both sides of Eq. (6) in spherical harmonics and matching the coefficients for each  $l$ , the equations for the radial functions may all be written in the form

$$[h_0(l) - \varepsilon_i^{(0)}] y_l(r) = f_l(r), \quad (8)$$

where

$$h_0(l) = -\frac{1}{2m} \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{l(l+1)}{2mr^2} - \frac{Ze^2}{r}$$

and  $\varepsilon_l^{(0)} = \varepsilon_0^{(0)}$  for even  $l$ ,  $\varepsilon_1^{(0)}$  for odd  $l$ . The functions  $f_l$  are easily computed, and the equations may be solved numerically. This calculation will be presented in the next section. Once the radial functions  $y_l$  are obtained, the first-order correction to the density in the Hartree approximation is found by adding the squared wave functions and collecting terms of order  $\lambda$ . The resulting density may be written in the form

$$n^{(1)}(\vec{r}) = n_0^{(1)}(r) Y_0^0(\vec{\Omega}) + n_2^{(1)}(r) Y_2^0(\vec{\Omega}) + n_4^{(1)}(r) Y_4^0(\vec{\Omega})$$

with

$$\begin{aligned} n_0^{(1)}(r) &= 2c_{00}^0 R_{10}(r) y_0(r) + 2c_{11}^0 R_{21}(r) y_1(r), \\ n_2^{(1)}(r) &= 2c_{02}^2 R_{10}(r) y_2(r) + 2c_{11}^2 R_{21}(r) y_1(r) \\ &\quad + 2c_{13}^2 R_{21}(r) y_3(r), \\ n_4^{(1)}(r) &= 2c_{13}^4 R_{21}(r) y_3(r). \end{aligned} \quad (9)$$

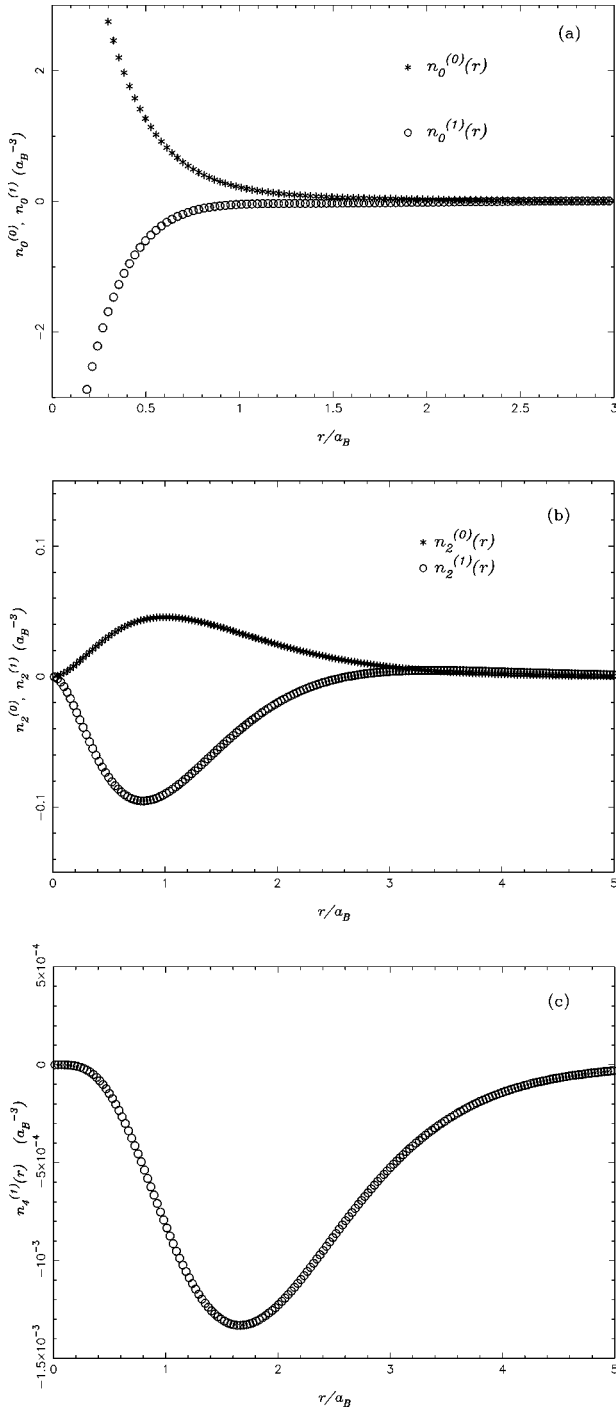


FIG. 1. Radial functions of the spherical harmonic decomposition of the density in the Hartree approximation in a helium  $P$  state. Zeroth and first-order corrections (designated by superscripts) in the electron-electron interaction are illustrated. Absolute magnitudes fall quickly with increasing spherical harmonic index  $l$  (designated by subscripts). (a)  $n_0^{(0)}(r)$ ,  $n_0^{(1)}(r)$ ; (b)  $n_2^{(0)}(r)$ ,  $n_2^{(1)}(r)$ ; (c)  $n_4^{(1)}(r)$ .

Note that to this order in  $\lambda$ , only one “offending” spherical harmonic  $Y_4^0(\vec{\Omega})$  appears. However, all even spherical harmonics would appear in higher orders in perturbation theory. Figure 1 illustrates the radial functions  $n_l^{(1)}(r)$  for the present model problem, as well as the analogous zeroth-order

densities  $n_l^{(0)}(r)$  appearing in the spherical harmonic decomposition of the density for the noninteracting problem [cf. Eq. (4)]. Note that the magnitude of the offending spherical harmonic component is quite small (ratio of maximum contribution to root mean-square density  $3.86 \times 10^{-3}$ ), and that the densities  $n_l^{(1)}(r)$  decrease very rapidly with increasing  $l$ . The reason for this is that at zeroth order, the density (of the noninteracting system) varies rather slowly as a function of the angular variable. When interactions are introduced, such a slowly varying potential has only a small amplitude for scattering electrons into high angular momentum states; the resulting density thus only has a small component of large  $l$  spherical harmonics. It is clear that this property is true at all orders in perturbation theory: the effective potential entering at any order will always have a much larger  $Y_0^0$  component than any other, leading to only small admixtures of high angular momenta in the wave functions. Finally, although we have illustrated this property in the specific context of a helium triplet  $P$  state, it should be quite general for atoms. Indeed, our model problem is in some sense a “worst-case” example; for larger atoms, particularly ones with many closed shells, the predominant spherical components of the density will be even larger. This helps to explain the success of using spherically averaged effective potentials in the Hartree approximation [7].

Spherical averaging is also a common practice in applying the Hartree-Fock approximation [9], and it is therefore of interest to assess the extent to which Eq. (1) will be violated without such averaging. We again proceed perturbatively. In addition to the direct potential  $U^{(1)}(\vec{r})$ , there is now a non-local exchange potential, to first order in perturbation theory, and the corrections to the wave functions take the form

$$\begin{aligned} \phi_0^{(1),HF} &= y_0^{HF}(r) Y_0^0(\vec{\Omega}) + y_2^{HF}(r) Y_2^0(\vec{\Omega}), \\ \phi_1^{(1),HF} &= y_1^{HF}(r) Y_1^0(\vec{\Omega}). \end{aligned} \quad (10)$$

There is no  $Y_3^0$  term in the wave functions because there is a precise cancellation between the direct and exchange terms. The resulting density, remarkably, has precisely the right form—Eq. (1)—to first order, unlike in the Hartree approximation. In fact, one may demonstrate that the solution to the HF approximation reproduces the correction to the density *exactly* to first order in the electron-electron interaction.

Unfortunately, this good property of the solutions to the HF equations is limited to first order in  $\lambda$ . This is most easily seen in the context of our model calculation for the He  $P$  state. The presence of a  $Y_2^0$  component to the density ensures that the effective potential seen by either electron has a similar component. For the  $\phi_0$  state, this leads to a contribution proportional to  $Y_2^0(\vec{\Omega})$ , as in Eq. (10). At second order in  $\lambda$ , this necessarily produces a component in the density proportional to  $Y_4^0(\vec{\Omega})$ . However, the fact that the HF density has the correct form to order  $\lambda$  implies that the magnitude of the violation will be even smaller than that found in the Hartree approximation.

### C. Harmonic content of the density in density-functional theory and local density approximation

The violations of Eq. (1) found in the Hartree and HF theories do *not* occur for the *exact* DFT, which, by construction, produces exact densities. In practice, one must always introduce approximations for the exchange-correlation energy and potential. To illustrate the point, we consider a perturbative application of the local density approximation (LDA) to our helium  $P$  state example.

The formalism closely parallels our perturbative approach to the Hartree approximation. In LDA, we need to solve self-consistently a Schrödinger's equation with an effective potential given by  $V_{eff}^H + V_{xc}^{LDA}$ , where  $V_{eff}^H$  is given by Eq. (5) and  $V_{xc}^{LDA} = \delta E_{xc}^{LDA}[n(\vec{r})]/\delta n(\vec{r})$ . For the purpose of this illustration, we neglect the correlation contribution and take  $V_{xc}^{LDA}(\vec{r}) \approx V_x(\vec{r}) = -[(6/\pi)n(\vec{r})]^{1/3}$  [14]. To first order in  $\lambda$ , it is sufficient to replace  $n$  in  $V_{xc}^{LDA}$  with  $n^{(0)}$ . Because  $V_{xc}^{LDA}$  is not an analytic function of the density, it is important to recognize that when  $V_{xc}^{LDA}$  is expanded in terms of spherical harmonics  $Y_l^0(\vec{\Omega})$ , the resulting series will involve all even values of  $l$ . This contrasts with the Hartree contribution, which at this order contained only  $l=0$  and  $l=2$  components. In some sense this suggests LDA will lead to stronger violations of Eq. (1) than we encountered in the Hartree approximation. However, the effective potential we construct at first order in  $\lambda$  is a slowly varying function of  $\vec{\Omega}$ , so that contributions from large values of  $l$  to the wave functions are still quite small.

When expanded in spherical harmonics, the corrections to the wave functions have a form very similar to Eq. (7), except  $\phi_0^{(1)}$  will now contain *all* even spherical harmonics, and  $\phi_1^{(1)}$  will contain all odd ones. Writing  $\phi_i^{(1)} = \sum_l y_{2l+i} Y_{2l+i}^0(\vec{\omega})$ , the equations satisfied by the  $y_{2l+i}$ 's are identical in form to Eq. (8), with a modified form for the inhomogeneous functions  $f_l$ . Once the radial functions have been obtained, the first-order correction to the density in LDA is given by  $n^{(1)}(\vec{r}) = \sum_l n_{2l}^{(1)}(r) Y_{2l}^0(\vec{\Omega})$  with

$$n_{2l}^{(1)}(r) = 2c_{0,2l}^{2l} R_{10}(r) y_{2l}(r) + 2c_{1,2l-1}^{2l} R_{21}(r) y_{2l-1}(r) + 2c_{1,2l+1}^{2l} R_{21}(r) y_{2l+1}(r).$$

In practice, the expansion of the density falls off so rapidly (see Fig. 2) with  $l$  that only the lowest few functions  $y_n$  need to be computed.

## III. RESTORING THE SYMMETRY OF THE DENSITY

### A. Constrained-search formulation

The calculations in the above sections to some extent explain why spherical averaging is successful in the Hartree and HF approximations, and in the LDA, when applied to atoms. Nevertheless, the averaging is basically *ad hoc*, and lacks a clear justification. From a formal point of view, spherical averaging has a dissatisfying aspect: the minimization principles that are used to derive the three approximations are abandoned when it is introduced. Formally, a more

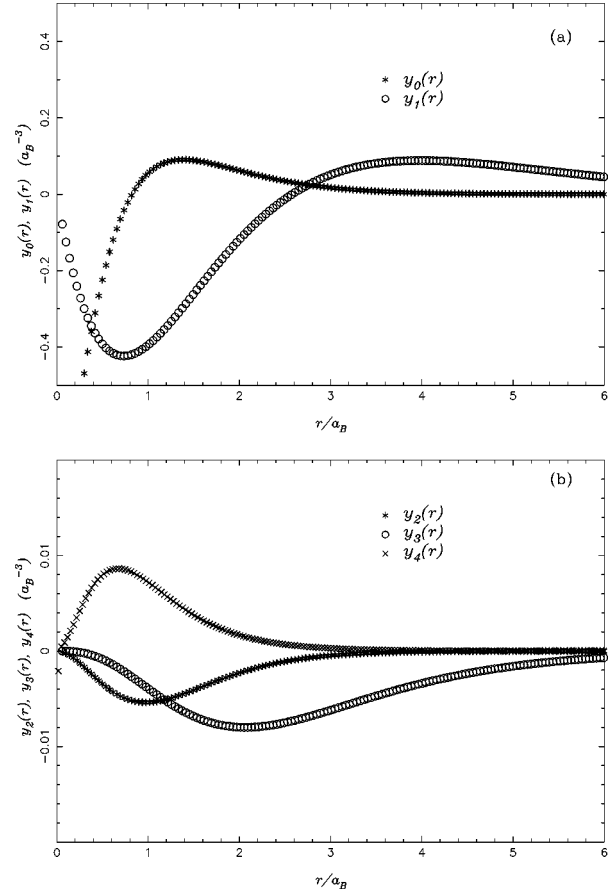


FIG. 2. Radial functions  $y_l(r)$  produced by the constrained Hartree approximation to first order in perturbation theory for a helium triplet  $P$  state (see text). (a)  $y_0(r)$ ,  $y_1(r)$ ; (b)  $y_2(r)$ ,  $y_3(r)$ ,  $y_4(r)$ . Note that the  $l=0,1,2$  contributions are identical to the results of the standard Hartree approximation;  $l=3,4$  results are modified by the constraint.

consistent approach—especially for DFT—is to modify, or more precisely, *constrain* the wave functions searched in the minimizations in such a way that Eq. (1) is guaranteed. This has the advantage that the energies of the atomic states found will be lower than those found by spherical averaging. In practice, however, the energy lowering turns out to be quite small. Nevertheless, it is useful to explore constrained-search methods for preserving symmetry properties of the density because such violations are known to occur in other symmetry properties—particularly those involving spin [15]—and may be responsible for more serious errors that arise in molecular calculations. The present formalism is an example of how to consistently impose symmetry on an approximate single-particle scheme.

As stated above, the Hartree, HF, and LDA equations are derived from minimization principles. In the Hartree approach, the energy functional is

$$E[\Psi] = \langle \Psi | H_0 | \Psi \rangle + \frac{e^2}{2} \int d^3r d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}. \quad (11)$$

Here,  $|\Psi\rangle$  is a normalized wave function,  $H_0$  is the nonin-

interacting electron Hamiltonian, and  $n(\vec{r})$  is the expectation value of the density in the state  $|\Psi\rangle$ . To generate the Hartree equations, one minimizes  $E[\Psi]$  among orthonormal product wave functions [7]. In density-functional theory, one adds an appropriate exchange-correlation energy  $E_{xc}$  to the expression (11), and then searches for the minimum of the resulting energy [14,16]. (This presumes the density is noninteracting  $v$ -representable, which we will assume for the states of interest.) For the exact exchange-correlation energy the resulting density satisfies Eq. (1). Of course, the exact exchange-correlation energy is unknown, and, in practice, one is forced to adopt approximations [14].

To constrain these searches to the subspace of states having a density of the form of Eq. (1), we introduce a set of  $r$ -dependent Lagrange multipliers  $\Lambda_{2l}(r)$ . The constraints that must be enforced are

$$\int d\vec{\Omega} n(\vec{r}) Y_{2l}^0(\vec{\Omega}) = 0, \quad 2l > 2L, \quad (12)$$

where  $L$  is the angular momentum of the state of interest. The functional we need to minimize is

$$E + E_{xc} + \int d^3r V_R(\vec{r}) n(\vec{r}), \quad (13)$$

where

$$V_R(\vec{r}) \equiv \sum_{l > 2L} \Lambda_{2l}(r) Y_{2l}^0(\vec{\Omega}). \quad (14)$$

After minimization of Eq. (13), we arrive at a single-particle Schrödinger equation

$$\left[ -\frac{1}{2m} \nabla^2 + v_s(\vec{r}) \right] \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}). \quad (15)$$

For density-functional theory,

$$v_s(\vec{r}) = -\frac{Ze^2}{r} + e^2 \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{xc}([n(\vec{r})], \vec{r}) + V_R(\vec{r}), \quad (16)$$

where  $V_{xc}$  is the exchange-correlation potential. For an  $N$ -electron atom, filling the lowest  $N$  eigenstates of Eq. (15) leads to the density used in Eq. (16), so these equations must be solved self-consistently. The Lagrange parameters  $\Lambda_{2l}(r)$  of Eq. (13) must be chosen to satisfy Eq. (12).

One natural, but incorrect, guess would be that  $V_R$  simply removes the high spherical harmonics present in the other terms entering  $v_s$ , rendering a spherically symmetric single-particle potential. This is not possible except for the trivial case of  $S$  states. For example, in our model calculation of the helium  $P$  state, the lowest spherical harmonic component present in  $V_R$  is  $l=4$ , which cannot remove the  $l=2$  component coming from the Hartree term. In fact, the single-particle potential in general contains *all* orders of spherical harmonics. With the exact form of  $V_{xc}$ ,  $V_R=0$ , but  $V_{xc}$  itself contains an infinite number of spherical harmonics. This is

demonstrated in a specific soluble model (Appendix A): two fermions in a harmonic trap, interacting via a repulsive quadratic potential. The exact eigenfunctions of this system may be written down explicitly, and in Appendix A we show (a) that the density of a  $P$  state cannot be produced by a noninteracting electron system in any spherically symmetric potential, and (b) that the unique single-particle potential reproducing this density (cf. the Hohenberg-Kohn theorem [5]) in a noninteracting system contains all even orders of spherical harmonics.

## B. Perturbative implementation

Our proposed solution to the problem of producing densities that have an appropriate form for orbital angular momentum eigenstates thus reduces to finding a self-consistent solution to Eqs. (12), (15), and (16). The following is a practical procedure: (1) Obtain the self-consistent Kohn-Sham solution with the given  $E_{xc}[n]$  and the self-consistent total potential  $v_s(\vec{r})$ . We expect that this will violate *weakly* the constraints (12), with the offending density components  $n_{2L+2}(r), n_{2L+4}(r), \dots$  being small. (2) The restoring potential,  $V_{R,2L+2}(r), V_{R,2L+4}(r), \dots$  is determined by solving the equation

$$\begin{pmatrix} -n_{2L+2}^0(r) \\ -n_{2L+4}^0(r) \\ -n_{2L+6}^0(r) \\ \vdots \end{pmatrix} = \int_0^\infty dr' r'^2 \mathbf{K}^{FF}([v_s(0)]; r, r') \begin{pmatrix} V_{R,2L+2}^0(r') \\ V_{R,2L+4}^0(r') \\ V_{R,2L+6}^0(r') \\ \vdots \end{pmatrix}, \quad (17)$$

where  $K^{FF}$  is the submatrix ( $l, l' > 2L$ ) of the linear density response function  $K_{l,l'}(r, r')$  corresponding to  $v_s(\vec{r})$ . (3) The new wave function and density, satisfying the constraints (12) are determined from  $v_s(\vec{r}) + V_R(\vec{r})$ .

Equivalently, this process can be carried out in terms of wave functions (see Appendix B). Perturbative energies for our helium  $P$  state example using the constrained Hartree approximation and LDA are presented in Table I along with comparable results for unconstrained and spherically averaged approaches.

## IV. CONCLUSION

This paper deals with the angular dependence of the electron density  $n(\vec{r})$  of an atom in a state of finite angular momentum  $L$ , both in the exact physical state and in various single-particle descriptions. The spherical harmonic content of the physical density, as a direct consequence of the Wigner-Eckart theorem, is limited to even values of  $l \leq 2L$ . However in the Hartree, Hartree-Fock, and the various ap-

proximate forms of Kohn-Sham theory, the spherical harmonic content of the density involves *all*  $l$  values (although components with  $l > 2L$  are small.) The exact Kohn-Sham effective single-particle potential by definition reproduces the  $l$ -limited physical density; on the other hand, the potential involves all  $l$  values. (This is documented for the case of an exactly soluble model of a harmonic atom with interacting electrons.)

We show how the requirement  $l \leq 2L$  can be restored by a constrained-search procedure using Lagrange parameter functions. Various numerical illustrations are presented.

Somewhat analogous symmetry violations are known to arise in connection with the electronic spin quantum numbers. They may be susceptible to similar analysis and symmetry restoration.

#### ACKNOWLEDGMENTS

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#### APPENDIX A: DENSITY FOR A HARMONIC ATOM

In this appendix, we present a calculation of a  $P$  state for two spinless fermions trapped in a quadratic potential, interacting via a repulsive quadratic potential. This is not intended as a realistic model of a physical atom, but it shares with physical atoms their symmetry properties and allows analytic calculations of wave functions and densities. Our main goals in this calculation are to demonstrate that (i) the exact density in this interacting state cannot be reproduced by noninteracting fermions in any spherically symmetric potential, and (ii) that the single-particle potential that *does* reproduce the density contains spherical harmonics of all even orders.

Our model Hamiltonian is

$$H = -\frac{1}{2m}[\nabla_1^2 + \nabla_2^2] + \frac{1}{2}m\omega_0^2[r_1^2 + r_2^2] - \frac{1}{2}m\omega_1^2|\vec{r}_1 - \vec{r}_2|^2. \quad (\text{A1})$$

Defining center-of-mass and relative coordinates  $\vec{r}_{cm} = (\vec{r}_1 + \vec{r}_2)/2$ ,  $\vec{r} = (\vec{r}_1 - \vec{r}_2)/2$ , this may be rewritten as a sum of commuting Hamiltonians, one for the center-of-mass coordinate ( $H_{CM}$ ) and one for relative coordinates ( $H_R$ ),

$$H_{CM} = -\frac{1}{2\mu}\nabla_{cm}^2 + \frac{1}{2}\mu\omega_0^2r_{cm}^2, \\ H_R = -\frac{1}{2\mu}\nabla^2 + \frac{1}{2}\mu\omega_R^2r^2, \quad (\text{A2})$$

where  $\mu = 2m$ ,  $\omega_R^2 = \omega_0^2 - \frac{1}{2}\omega_1^2$ . The total angular momentum operator may be written in the form  $\vec{L} = \vec{L}_{CM} + \vec{L}_R$ , the sum of angular momentum operators for the center-of-mass and relative coordinates. Using the composition rules for angular

momenta [13], it is easy to see that the  $P$  state of lowest energy is formed by putting the center-of-mass degree of freedom in an  $s$  state and the relative degree of freedom in a  $p$  state. Using the explicit forms for harmonic oscillator states, the wave function is

$$\Psi = \left\{ \left[ \frac{1}{\pi l_{CM}^2} \right]^{3/4} \exp \left[ -\frac{r_{cm}^2}{2l_{CM}^2} \right] \right\} \left\{ \frac{1}{\sqrt{2}} \left[ \frac{1}{\pi l^2} \right]^{3/4} \right. \\ \left. \times H_1 \left( \frac{z}{l} \right) \exp \left[ -\frac{r^2}{2l^2} \right] \right\}, \quad (\text{A3})$$

where  $H_1(x) = 2x$  is a Hermite polynomial,  $l^2 = (\mu\omega_R)^{-1}$ , and  $l_{CM}^2 = (\mu\omega_0)^{-1}$ . The density of this state is

$$n(\vec{r}) = [A + Bz^2] e^{-r^2/L^2} \\ = \left\{ \left[ A + \frac{1}{3}Br^2 \right] + \frac{B}{3} \sqrt{\frac{16\pi}{5}} r^2 Y_2^0(\vec{\Omega}) \right\} e^{-r^2/L^2} \quad (\text{A4})$$

with

$$A = 4\pi^{3/2}\xi^5 C^2, \\ B = (4\pi)^{3/2} \frac{\xi^3 l^4}{L^4} C^2. \quad (\text{A5})$$

The length scales appearing in the above two equations are given by  $L^2 = l^2 + l_{CM}^2$  and  $\xi^{-2} = l_{CM}^{-2} + l^{-2}$ , and  $C = [\pi l_{CM} l]^{-3/2} [\sqrt{2}l]^{-1}$ . Note that Eq. (A4) has the form required by Eq. (1).

We now demonstrate that Eq. (A4) is not derivable from a system of *noninteracting* fermions in a spherically symmetric external potential. To show this, suppose the density *was* derivable from such a potential. Then the two occupied single-particle states would necessarily have the form  $\phi_0(\vec{r}) = S(r)Y_0^0(\vec{\Omega})$ ,  $\phi_1(\vec{r}) = P(r)Y_1^0(\vec{\Omega})$ . The sum of the squares of these gives the density; matching this to Eq. (A4) gives explicit expressions for  $S(r)$  and  $P(r)$ ,

$$S(r) = \sqrt{4\pi A} e^{-r^2/2l^2}, \\ P(r) = \left[ \frac{B}{3c_{11}^2} \sqrt{\frac{16\pi}{5}} \right]^{1/2} r e^{-r^2/2l^2}. \quad (\text{A6})$$

It is interesting to notice that the functional forms of  $S$  and  $P$  are perfectly compatible with a state of noninteracting fermions in a harmonic trapping potential. However, the *normalizations* of  $S$  and  $P$  are not correct. For example,  $S(r)$  is properly normalized if and only if  $A = (\pi L^2)^{3/2}$ . An examination of the explicit expression for  $A$ , Eq. (A5), reveals that this is the case only if  $\omega_1 = 0$ ; i.e., the repulsion vanishes. Thus, for noninteracting fermions, *no* spherical potential will reproduce the interacting density.

On the other hand, a noninteracting potential that is not spherically symmetric can be found to make the density of

two noninteracting fermions take the form of Eq. (A4). We again demonstrate this by using perturbation theory. Because the density is axially symmetric—i.e., it may be written as a function of  $r$  and  $z$ —we look for an effective potential that is also axially symmetric. In the body of this paper we have essentially expressed the  $z$  dependence of densities and potentials in terms of spherical harmonics. However, in this appendix, because harmonic oscillator wave functions have a number of useful algebraic properties, we expand instead in powers of  $z$ .

The form of Eq. (A4) suggests that the effective single-particle potential that reproduces the density has the form

$$V_{eff}(\vec{r}) = \frac{1}{2} m \omega_{eff}^2 r^2 + \delta V(z),$$

where  $\omega_{eff} = 1/\mu L^2$ . We will perform our perturbation theory around a  $V_{eff}$  with  $\delta V = 0$ ; this is slightly different than working around the noninteracting state, as the length scale  $L$  is modified by interactions. Nevertheless, it is clear that  $\delta V$  must be small if the interaction strength is weak. For this form of the potential, it is also clear that the two single-particle states must have the form

$$\phi_i(\vec{r}) = \psi_0(x) \psi_0(y) \chi_i(z) \quad (\text{A7})$$

with  $i=0,1$ , and  $\psi_0$  the ground state of a one-dimensional harmonic oscillator with frequency  $\omega_{eff}$ , and for  $\delta V=0$ ,  $\chi_0(z) \equiv \psi_0(z)$  may be taken as a harmonic oscillator ground state and  $\chi_1(z) \equiv \psi_1(z)$  as the first excited state. If the electrons were noninteracting, we would necessarily have in Eq. (A4):

$$A = A_0 \equiv \left[ \frac{1}{\pi L^2} \right]^{3/2},$$

$$B = B_0 \equiv \left[ \frac{1}{\pi L^2} \right]^{3/2} \frac{2}{L^2}. \quad (\text{A8})$$

It is convenient to parametrize the effect of interactions in terms of the deviations of  $A$  and  $B$  from these values,

$$\delta n(\vec{r}) \equiv [\delta A + \delta B z^2] e^{-r^2/L^2}$$

with  $\delta A \equiv A - A_0$ ,  $\delta B \equiv B - B_0$ . Denoting the first-order corrections to  $\chi_i(z)$  as  $\delta \chi_i(z)$ , it is easy to demonstrate to lowest order in perturbation theory that

$$[\delta \tilde{A} + \delta \tilde{B} z^2] e^{-z^2/2L^2} = \delta \chi_0(z) + \sqrt{2} \frac{z}{L} \delta \chi_1(z), \quad (\text{A9})$$

where  $(\delta \tilde{A}, \delta \tilde{B}) = (\pi L^2)^{5/4} (\delta A, \delta B)/2$ . With some algebra, Eq. (A9) may be written as

$$\delta \chi_0(z) + \sqrt{2} \frac{z}{L} \delta \chi_1(z) = \beta \psi_2(z), \quad (\text{A10})$$

where  $\beta = (2^{3/2}/6)(\pi L^2)^{1/4} [\delta \tilde{B} L^2 - \delta \tilde{A}]$ , and  $\psi_2(z)$  is the  $n=2$  harmonic-oscillator state.

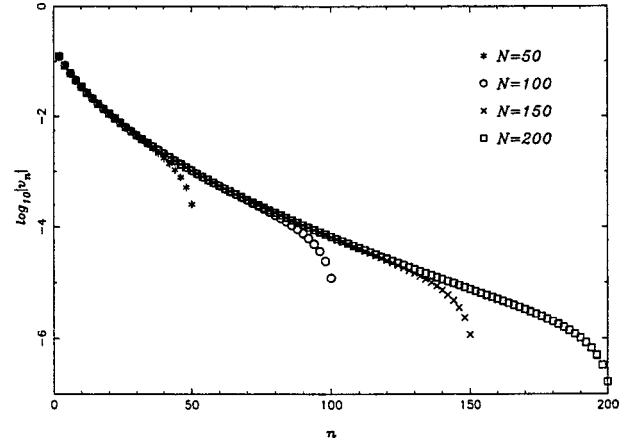


FIG. 3. Approximate coefficients  $v_n$  in expansion of  $\delta V$  given by Eq. (A13) for  $\beta=0.1$  (see text).  $v_n$  is assumed to vanish for  $n > N$  with different values of  $N$  given in the figure. The expansion coefficients converge to a unique set of values as  $N \rightarrow \infty$ .

We now expand  $\delta \chi_0(z), \delta \chi_1(z)$  in harmonic-oscillator states:

$$\delta \chi_0(z) = \sum_{n=0}^{\infty} c_{2n} \psi_{2n}(z),$$

$$\delta \chi_1(z) = \sum_{n=0}^{\infty} c_{2n+1} \psi_{2n+1}(z). \quad (\text{A11})$$

The coefficients  $c_n$  obey the recursion relation

$$\sqrt{n+1} c_{n+1} = \beta \delta_{n,2} - c_n - \sqrt{n} c_{n-1} \quad (\text{A12})$$

for  $n \geq 2$ . In addition,  $c_0, c_1 = 0$  since  $\delta \chi_0(z), \delta \chi_1(z)$  must be orthogonal to  $\chi_0, \chi_1$ .

Perturbation theory defines  $\delta \chi_0, \delta \chi_1(z)$  in terms of  $\delta V$ . A useful expansion for  $\delta V$  is

$$\delta V(z) = \sum_{n \text{ even}} \frac{v_n}{2^{n/2} \sqrt{n!}} H_n \left( \frac{z}{L} \right). \quad (\text{A13})$$

First-order perturbation theory yields a linear relation between the  $c_n$ 's and the  $v_n$ 's,

$$c_n = \begin{cases} \frac{v_n}{n \omega_{eff}} & n \text{ even} \\ \frac{\sqrt{n+1} v_{n+1} + \sqrt{n} v_{n-1}}{(n-1) \omega_{eff}} & n \text{ odd}; \end{cases} \quad (\text{A14})$$

Eqs. (A12) and (A14) may be combined to form a set of recursion relations for  $v_n$ . Any choice of  $v_2$  will generate an entire set of  $v_n$ 's, whose magnitude in general grows rapidly with  $n$ . The resulting  $\delta V(z)$  is ill-defined. However, for a given  $\beta$  there is a *unique* choice of  $v_2$  for which  $|v_n|$  uniformly decreases with increasing even  $n$ . (Note that  $v_n$  vanishes for odd values of  $n$  and  $v_{2m}$  alternates in sign.) This choice may be found as follows: select a large value of  $N$  and set  $v_n = 0$  for  $n > N$ . The recursion relations for  $v_n$  ( $0 < n$



$\leq N$ ) then may be written as a matrix equation that may be solved numerically with little difficulty. Figure 3 illustrates  $v_n$  for  $\beta=0.1$  and several increasing values of  $N$ . As may be seen, the  $v_n$  converge to a *unique* sequence as  $N \rightarrow \infty$ , and the limiting values vanish rapidly with increasing  $n$ .

The potential we have found is the *unique* single-particle potential that produces the density of the harmonic atom model, to first order in perturbation theory, as required by the Hohenberg-Kohn theorem [5]. It involves all even powers of  $z$ , or, equivalently, all spherical harmonics  $Y_{2l}^0$ . This demonstrates that, to reproduce the physical density, involving  $l=0$  and  $l=2$  only, requires, in the absence of interactions, an external potential involving all even  $l$  values.

### APPENDIX B: PERTURBATIVE CALCULATION OF DENSITIES AND ENERGIES FOR CONSTRAINED ENERGY FUNCTIONAL

In this appendix, we discuss a concrete example of the ideas developed in Sec. III, providing details of how, for the helium  $P$  state, our perturbative Hartree approximation is modified by the introduction of the constraint.

We begin with the single-particle Schrödinger equation, (15), with single-particle potential

$$v_s(\vec{r}) = \frac{-Ze^2}{r} + \lambda e^2 \int d^3r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + \lambda V_R(\vec{r}). \quad (\text{B1})$$

To lowest nontrivial order in  $\lambda$ , the corrections to the wave functions  $\phi_i^{(1)}$  obey Eq. (6). The form of  $U^{(1)}$  must be modified to include the restoring potential

$$U^{(1)}(\vec{r}) \rightarrow U_R^{(1)}(\vec{r}) \equiv e^2 \int d^3r' \frac{n^{(0)}(\vec{r}')}{|\vec{r}-\vec{r}'|} + V_R(\vec{r}).$$

Note that to this order in perturbation theory, the  $l=0$  and  $l=2$  components in a spherical harmonic expansion of  $U_R^{(1)}(\vec{r})$  come only from the Hartree potential, and so are identical to the ones encountered in Sec. II B. The higher  $l$  components of  $U_R^{(1)}$  come only from  $V_R$ .  $U_R^{(1)}(\vec{r})$  thus can be expanded as

$$U_R^{(1)}(\vec{r}) = \Phi_0^{(1)}(r)Y_0^0(\vec{\Omega}) + \Phi_2^{(1)}(r)Y_2^0(\vec{\Omega}) + v_4(r)Y_4^0(\vec{\Omega}) + v_6(r)Y_6^0(\vec{\Omega}) + \dots$$

The radial functions  $\Phi_n^{(1)}$  are determined fully by the noninteracting electron density, and the functions  $v_n(r)$  come from  $V_R$ .

Because all even values of  $l$  appear in the decomposition of  $U_R^{(1)}$ , the corrections to the wave functions contain all spherical harmonics:

$$\begin{aligned} \phi_0^{(1)} &= y_0(r)Y_0^0(\vec{\Omega}) + y_2(r)Y_2^0(\vec{\Omega}) + y_4(r)Y_4^0(\vec{\Omega}) + \dots, \\ \phi_1^{(1)} &= y_1(r)Y_1^0(\vec{\Omega}) + y_3(r)Y_3^0(\vec{\Omega}) + y_5(r)Y_5^0(\vec{\Omega}) + \dots \end{aligned} \quad (\text{B2})$$

TABLE I. Zeroth ( $E^{(0)}$ ), first- ( $\lambda E^{(1)}$ ), and second- ( $\lambda^2 E^{(2)}$ ) order contributions to the He  $2P$  state energy calculated in perturbation theory in the electron-electron interaction strength  $\lambda$  by various methods.  $H$ , Hartree approximation;  $H-Sph$ , spherically averaged Hartree approximation;  $H-C$ , constrained Hartree approximation;  $LDA$ , local density approximation;  $LDA-C$ , constrained local density approximation. Energy units are  $e^2/a_B$  with  $a_B = \hbar^2/me^2$  the hydrogenic Bohr radius.

	$H$	$H-Sph$	$H-C$	$LDA$	$LDA-C$
$E^{(0)}$	-2.5000	-2.5000	-2.5000	-2.5000	-2.5000
$E^{(1)}$	1.3063	1.3063	1.3063	0.5439	0.5439
$E^{(2)}$	-0.4059	-0.4039	-0.4052	-0.1140	-0.1139

Noting that the radial functions  $y_l(r)$  fall off very rapidly with  $l$ , we retain only  $l \leq 4$  in the calculations that follow. The radial functions  $y_l$  obey Eq. (8), with

$$\begin{aligned} f_0(r) &= [\varepsilon_0^{(1)} - c_{00}^0 \Phi_0^{(1)}(r)]R_{10}(r), \\ f_1(r) &= [\varepsilon_1^{(1)} - c_{01}^1 \Phi_0^{(1)}(r) - c_{21}^1 \Phi_2^{(1)}(r)]R_{21}(r), \\ f_2(r) &= -c_{20}^2 \Phi_2^{(1)}(r)R_{10}(r), \\ f_3(r) &= -c_{21}^3 \Phi_2^{(1)}(r)R_{21}(r) - c_{41}^3 v_4(r)R_{21}(r), \\ f_4(r) &= -c_{40}^4 v_4(r)R_{10}(r). \end{aligned} \quad (\text{B3})$$

Only  $f_3$  and  $f_4$  are modified by  $V_R$ ; it follows that the  $y_0$ ,  $y_1$ , and  $y_2$  are identical to the results of the Hartree approximation without the constraint. The equations to be solved are closed by requiring the highest spherical harmonic component retained,  $l=4$ , to vanish to first order in  $\lambda$  in the density:

$$n_4^{(1)}(r) = c_{04}^4 R_{10}(r)y_4(r) + c_{31}^4 R_{21}(r)y_3(r) = 0. \quad (\text{B4})$$

The constrained Hartree state is found by solving Eqs. (8), (B3), and (B4). The radial functions  $y_n(r)$  results are presented in Fig. 3. We present in Table I the energies obtained by the Hartree approximation, the spherically averaged Hartree approximation, and the constrained Hartree approximation. As can be seen, the differences among the three approaches only arise at order  $\lambda^2$  [17], and are quite small. Nevertheless, the constrained Hartree approximation yields an energy considerably closer to the unconstrained Hartree approximation than the spherically averaged one, indicating that imposing the symmetry by spherical averaging raises the energy considerably more than necessary.

Finally, for comparison we also present in Table I analogous energies for the results of a constrained, perturbative LDA calculation. The method for computing the wave functions is, *mutatis mutandis*, the same as for the constrained Hartree approximation. As in that approximation, the introduction of the constraint introduces little change in the energy.

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