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Restricted Hartree–Fock calculations have been performed on the Fermi configurations of n electrons confined within a cube. The self-consistent-field orbitals have been expanded in a basis of N particle-in-a-box wave functions. The difficult one- and two-electron integrals have been reduced to a small set of canonical integrals that are calculated accurately using quadrature. The total energy and exchange energy per particle converge smoothly toward their limiting values as n increases; the highest occupied molecular orbital–lowest unoccupied molecular orbital gap and Dirac coefficient converge erratically. However, the convergence in all cases is slow. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1873552]

I. INTRODUCTION

Jellium is the most popular electronic structure model in solid-state physics and also constitutes the starting point for many of the density functional theories that are now widely used in computational chemistry.[1] Its success stems largely from its surpassing simplicity: an infinite uniform gas of electrons characterized by a single number, its electron density ρ. The original idea, particulate electrons moving in a background of uniform positive charge, was introduced[2] by Kelvin soon after the discovery of the electron and was quickly adopted by Thomson in his "plum pudding" model of atomic structure.[3] Although it fell out of favor following Rutherford's discovery of the nucleus, it was subsequently revived in the "statistical" quantum mechanical models of Thomas,[4] Fermi,[5] Bloch,[6] and Dirac[7] who determined the exact kinetic energy and exchange energy of jellium, as functions of ρ. The ρ dependence of the correlation energy of jellium proved more difficult to determine and produced an impressive body of work by Wigner,[8] Gell-Mann and Brueckner,[9] Carr,[10,11] and Nozières and Pines[12] before the definitive quantum Monte Carlo calculations[13,14] of Ceperley and Alder and their parametrization by Vosko, Wilk, and Nusair.[15] As a result, the properties of jellium are now well established, in the low-density limit,[8,10,12] the high-density limit,[9,11] and for intermediate densities in both ferromagnetic and paramagnetic states.[13–15]

Jellium has continued to underpin a wide array of simple models for complex physical and chemical systems and is widely used, for example, in theoretical electrochemistry.[16] However, there has also been a resurgence of interest in the quantum mechanical treatment of Kelvin–Thomson models wherein a *finite* number n of electrons move freely within a finite space. Ellert *et al.*, for example, have rationalized[17] the optical absorption spectra of small, open-shell sodium clusters by considering n electrons in a spheroidal cavity, Koskinen, Lipas, and Manninen have studied n electrons in a relaxed background charge density,[18] Holas *et al.* have examined n electrons in a magnetic field,[19] and Alavi's group has recently published studies of $n=2$ highly correlated electrons in a cube[20] and a ball.[21]

Inspired by these studies, we have embarked upon a systematic study of the properties of n electrons confined within a cube, with a background of uniform positive charge, a neutral system that we will call "finite jellium." In this paper, we report the results of restricted Hartree–Fock (RHF) calculations where the orbitals are expanded in a basis of N particle-in-a-box functions. We have examined the behavior of several properties [the total energy, the Fock exchange energy, the Dirac exchange energy, the density variance, and the HOMO-LUMO gap (HOMO and LUMO represent highest occupied and lowest unoccupied molecular orbitals, respectively)] as functions of n and N, and we have examined the convergence of these properties as n and N increase.

The following section describes the physical model and basis set that we have chosen and outlines the symmetry aspects of our calculations. After this, we present the RHF theory of our system and propose a numerical approach to the difficult Coulomb integrals that arise. We conclude with a discussion of some of the results that we have obtained. Atomic units are used throughout.

II. MODEL, BASIS SET, AND SYMMETRY

Our system consists of n electrons in a cube of length π within which there is uniformly distributed positive charge sufficient to make the system neutral. Thus, the Hamiltonian is

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TABLE I. Irreducible representations of O_h spanned by a set $\{a,b,c\}$ of basis functions.

Parities[a,b]	Representations
$E\ E\ E$	A_{1g}
$E\ E\ E'$	$A_{1g}+E_g$
$E\ E'\ E''$	$A_{1g}+A_{2g}+2E_g$
$E\ O\ O$	T_{2g}
$E\ O\ O'$	$T_{1g}+T_{2g}$
$O\ O\ O$	A_{2u}
$O\ O\ O'$	$A_{2u}+E_u$
$O\ O'\ O''$	$A_{1u}+A_{2u}+2E_u$
$O\ E\ E$	T_{1u}
$O\ E\ E'$	$T_{1u}+T_{2u}$

[a]E and O represent even and odd Cartesian parity, respectively.
[b]Single and double primes imply *distinct* quantum numbers.

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 + \frac{1}{2}\int\int_V \frac{(n/\pi^3)^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'$$

$$-\sum_{i=1}^{n}\int_V \frac{(n/\pi^3)}{|\mathbf{r}_i-\mathbf{r}|}d\mathbf{r} + \sum_{i<j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}, \quad (2.1)$$

where V indicates the region within the cube. The first term arises from the kinetic energy of the electrons, the second from the self-interaction of the positive charge, the third from the attraction between the positive charge and the electrons, and the fourth from interelectronic repulsions. The self-interaction term does not depend on the electron coordinates and, like the nuclear repulsion energy in a molecular calculation, can be treated as a constant.

The Schrödinger equation associated with Eq. (2.1) cannot be solved exactly but it can be treated approximately using RHF theory within a finite basis set. The natural basis functions are the normalized particle-in-a-box wave functions

$$\phi_m(\mathbf{r}) = (2/\pi)^{3/2}\sin(m_x x)\sin(m_y y)\sin(m_z z)$$

$$(0 \leqslant x,y,z \leqslant \pi) \quad (2.2)$$

(where the quantum numbers m_x, m_y, and m_z are positive integers) and it is convenient to order these functions according to their energies

$$2E_m = (m_x^2 + m_y^2 + m_z^2) = m^2. \quad (2.3)$$

We will use $\{a,b,c\}$ to refer to the set of symmetry-equivalent basis functions with quantum numbers a, b, and c. For example, $\{1,1,1\}\equiv\{\phi_{111}\}$, $\{2,1,1\}\equiv\{\phi_{211},\phi_{121},\phi_{112}\}$, and $\{1,3,5\}\equiv\{\phi_{135},\phi_{153},\phi_{315},\phi_{351},\phi_{513},\phi_{531}\}$. Each such set spans one, two, or three irreducible representations of the octahedral group O_h and it can be shown that these depend only on the parities of the integers a, b, and c. All ten cases that arise are shown in Table I. For example, the $\{1,1,1\}$ set transforms as A_{1g}, the $\{2,1,1\}$ set as T_{1u}, and the $\{1,3,5\}$ set as $A_{1g}+A_{2g}+2E_g$. Table II lists the first 178 basis functions, together with their energies and symmetries.

TABLE II. Energies m^2 and symmetries Γ of the particle-in-a-box wave functions.

i	ϕ_i	m^2	Γ
1	$\{1,1,1\}$	3	A_{1g}
2–4	$\{2,1,1\}$	6	T_{1u}
5–7	$\{2,2,1\}$	9	T_{2g}
8–10	$\{3,1,1\}$	11	$A_{1g}+E_g$
11	$\{2,2,2\}$	12	A_{2u}
12–17	$\{3,2,1\}$	14	$T_{1u}+T_{2u}$
18–20	$\{3,2,2\}$	17	T_{2g}
21–23	$\{4,1,1\}$	18	T_{1u}
24–26	$\{3,3,1\}$	19	$A_{1g}+E_g$
27–32	$\{4,2,1\}$	21	$T_{1g}+T_{2g}$
33–35	$\{3,3,2\}$	22	T_{1u}
36–38	$\{4,2,2\}$	24	$A_{2u}+E_u$
39–44	$\{4,3,1\}$	26	$T_{1u}+T_{2u}$
45	$\{3,3,3\}$	27	A_{1g}
46–48	$\{5,1,1\}$	27	$A_{1g}+E_g$
49–54	$\{4,3,2\}$	29	$T_{1g}+T_{2g}$
55–60	$\{5,2,1\}$	30	$T_{1u}+T_{2u}$
61–63	$\{4,4,1\}$	33	T_{2g}
64–66	$\{5,2,2\}$	33	T_{2g}
67–69	$\{4,3,3\}$	34	T_{1u}
70–75	$\{5,3,1\}$	35	$A_{1g}+A_{2g}+2E_g$
76–78	$\{4,4,2\}$	36	$A_{2u}+E_u$
79–84	$\{5,3,2\}$	38	$T_{1u}+T_{2u}$
85–87	$\{6,1,1\}$	38	T_{1u}
88–93	$\{6,2,1\}$	41	$T_{1g}+T_{2g}$
94–96	$\{4,4,3\}$	41	T_{2g}
97–102	$\{5,4,1\}$	42	$T_{1u}+T_{2u}$
103–105	$\{5,3,3\}$	43	$A_{1g}+E_g$
106–108	$\{6,2,2\}$	44	$A_{2u}+E_u$
109–114	$\{5,4,2\}$	45	$T_{1g}+T_{2g}$
115–120	$\{6,3,1\}$	46	$T_{1u}+T_{2u}$
121	$\{4,4,4\}$	48	A_{2u}
122–127	$\{6,3,2\}$	49	$T_{1g}+T_{2g}$
128–133	$\{5,4,3\}$	50	$T_{1u}+T_{2u}$
134–136	$\{5,5,1\}$	51	$A_{1g}+E_g$
137–139	$\{7,1,1\}$	51	$A_{1g}+E_g$
140–145	$\{6,4,1\}$	53	$T_{1g}+T_{2g}$
146–151	$\{7,2,1\}$	54	$T_{1u}+T_{2u}$
152–154	$\{5,5,2\}$	54	T_{1u}
155–157	$\{6,3,3\}$	54	T_{1u}
158–163	$\{6,4,2\}$	56	$A_{1u}+A_{2u}+2E_u$
164–166	$\{7,2,2\}$	57	T_{2g}
167–169	$\{5,4,4\}$	57	T_{2g}
170–172	$\{5,5,3\}$	59	$A_{1g}+E_g$
173–178	$\{7,3,1\}$	59	$A_{1g}+A_{2g}+2E_g$

The theory below is easily extended to cubes of any size. The Coulomb integrals that arise in a cube of length $h\pi$ can be formed from the canonical values simply by dividing by h and, likewise, the kinetic energy integrals can be obtained by dividing by h^2.

III. SCF THEORY

If n is even, the RHF wave function for our system is the Slater determinant

TABLE III. Number of distinct, nonvanishing $(\mathbf{p}|\mathbf{q})$ integrals with $0 \leqslant p_i, q_i \leqslant 2m$.

m	0	1	2	3	4	5
Number	1	20	165	816	2925	8436
m	6	7	8	9	10	11
Number	20 825	45 760	91 881	171 700	302 621	508 080
m	12	13	14	15	16	17
Number	818 805	1 274 196	1 923 825	2 829 056	4 064 785	5 721 300

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(1) & \bar{\psi}_1(1) & \psi_2(1) & \cdots & \bar{\psi}_{n/2}(1) \\ \psi_1(2) & \bar{\psi}_1(2) & \psi_2(2) & \cdots & \bar{\psi}_{n/2}(2) \\ \psi_1(3) & \bar{\psi}_1(3) & \psi_2(3) & \cdots & \bar{\psi}_{n/2}(3) \\ \vdots & \vdots & \vdots & & \vdots \\ \psi_1(n) & \bar{\psi}_1(n) & \psi_2(n) & \cdots & \bar{\psi}_{n/2}(n) \end{vmatrix}. \quad (3.1)$$

If all Coulomb interactions in Eq. (2.1) are neglected, the orbitals ψ_i are just the first $n/2$ of the basis functions ϕ_m in Table II. We will refer to this as the Fermi configuration. If repulsion is included, the orbitals can no longer be found in closed form, but can still be expanded in the ϕ_m basis, i.e.,

$$\psi_a = \sum_m c_{ma} \phi_m, \quad (3.2)$$

and the resulting total energy is[22]

$$E = \frac{n^2}{2} E_0 + \sum_{\mathbf{ab}} P_{\mathbf{ab}}(T_{\mathbf{ab}} + nV_{\mathbf{ab}})$$

$$+ \frac{1}{2} \sum_{\mathbf{abcd}} \left[P_{\mathbf{ab}} P_{\mathbf{cd}} - \frac{1}{2} P_{\mathbf{ad}} P_{\mathbf{bc}} \right] (\mathbf{ab}|\mathbf{cd}), \quad (3.3)$$

where we have introduced the total density matrix $\mathbf{P}$, the unit self-interaction energy

$$E_0 = \frac{1}{\pi^6} \int \int_V \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 \, d\mathbf{r}_2, \quad (3.4)$$

the kinetic energy integrals

$$T_{\mathbf{ab}} = \frac{\delta_{\mathbf{ab}}}{2}(a_x^2 + a_y^2 + a_z^2), \quad (3.5)$$

the attraction integrals

$$V_{\mathbf{ab}} = -\frac{1}{\pi^3} \int \int_V \frac{\phi_{\mathbf{a}}(\mathbf{r}_1)\phi_{\mathbf{b}}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 \, d\mathbf{r}_2, \quad (3.6)$$

and the two-electron integrals

$$(\mathbf{ab}|\mathbf{cd}) = \int \int_V \frac{\phi_{\mathbf{a}}(\mathbf{r}_1)\phi_{\mathbf{b}}(\mathbf{r}_1)\phi_{\mathbf{c}}(\mathbf{r}_2)\phi_{\mathbf{d}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 \, d\mathbf{r}_2. \quad (3.7)$$

The Fock matrix elements required for the SCF procedure are given[22] by

$$F_{\mathbf{ab}} = T_{\mathbf{ab}} + nV_{\mathbf{ab}} + \sum_{\mathbf{cd}} P_{\mathbf{cd}} \left[(\mathbf{ab}|\mathbf{cd}) - \frac{1}{2}(\mathbf{ad}|\mathbf{bc}) \right] \quad (3.8)$$

and we have written a program that assembles the required integrals from a relatively small number of canonical inte-

grals (see below) and solves the Roothaan–Hall equations[23,24] by Pulay's direct inversion in the iterative subspace (DIIS) extrapolation procedure.[25]

To use the program, the user specifies n, N, and the mean electron density $\langle \rho \rangle$ and then stipulates the desired symmetries of the occupied orbitals. For example, one would specify a calculation of the Fermi configuration for 16 electrons as $2A_{1g} + T_{1u} + T_{2g}$. The program then uses the initial guess $\mathbf{P} = \mathbf{0}$ and, after each SCF cycle, fills the lowest orbitals of the requested symmetry. The SCF procedure usually converges rapidly, although the $n=126$ and $n=142$ cases converge relatively slowly because of the competing T_{2g} sets and competing E_g sets, respectively. Convergence is declared when the norm of the DIIS error matrix reaches 10^{-5}.

Unless n is small, there are often several low-lying RHF states with comparable energies. For example, for $n=16$, $N=178$, and $\langle \rho \rangle = 1$, we find two states with energies

$$E(1a_{1g}^2 1t_{1u}^6 1t_{2g}^6 2a_{1g}^2) = 84.694\,650, \quad (3.9)$$

$$E(1a_{1g}^2 1t_{1u}^6 1t_{2g}^6 1a_{2u}^2) = 84.678\,759, \quad (3.10)$$

and the Fermi configuration (3.9) lies significantly higher than the non-Fermi configuration (3.10). As n grows, it becomes increasingly difficult to locate the ground state with certainty and, to avoid this quagmire, we decided always to use the Fermi configuration, even though the example above shows that this strategy sometimes yields a low-lying excited state. Since we also wish to avoid the problems associated with partially occupied degenerate orbitals, we have confined our attention to values of n that yield completely filled shells.

IV. COULOMB INTEGRALS

One can use the trigonometric identity

$$2 \sin ax \sin bx = \cos(a - b)x - \cos(a + b)x \quad (4.1)$$

to reduce E_0, V_{ab} and $(\mathbf{ab}|\mathbf{cd})$ to linear combinations of *canonical* integrals of the form

$$(\mathbf{p}|\mathbf{q}) = \pi^{-6} \int \int_V \frac{\cos(p_x x_1)\cos(p_y y_1)\cos(p_z z_1)\cos(q_x x_2)\cos(q_y y_2)\cos(q_z z_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 \, d\mathbf{r}_2, \tag{4.2}$$

where the p_i and q_i are non-negative integers. Whereas the number of $(\mathbf{ab}|\mathbf{cd})$ increases as N^4, the number of $(\mathbf{p}|\mathbf{q})$ grows only as N^2. This is a major practical advantage because it allows us to hold all $(\mathbf{p}|\mathbf{q})$ in memory, even when N is large, and then calculate $(\mathbf{ab}|\mathbf{cd})$, as needed, on the fly. $(\mathbf{p}|\mathbf{q})$ possess 48-fold permutational symmetry and, moreover, $(\mathbf{p}|\mathbf{q})$ vanishes unless p_x+q_x, p_y+q_y, and p_z+q_z are all even. It is worth exploiting these symmetry properties fully and it can be shown that there are $m^2(m^2+1)(m^2+2)/6$ distinct, nonzero $(\mathbf{p}|\mathbf{q})$ with indices p_i and q_i not exceeding $2m-2$. A few examples of this are given in Table III. Although the number is manageable if m is not too large, it remains important to develop efficient algorithms for calculating the $(\mathbf{p}|\mathbf{q})$ and we have explored several approaches to this.

In our first approach, we apply the Fourier identity

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \pi^{-2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} r^{-2}$$
$$\times \exp[2i\mathbf{r} \cdot (\mathbf{r}_1 - \mathbf{r}_2)] dx \, dy \, dz \tag{4.3}$$

to reduce Eq. (4.2) to the three-dimensional integral

$$(\mathbf{p}|\mathbf{q}) = \pi^{-3} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{f_{p_x q_x}(x) f_{p_y q_y}(y) f_{p_z q_z}(z)}{x^2 + y^2 + z^2} dx \, dy \, dz, \tag{4.4}$$

$$f_{pq}(x) = \begin{cases} \dfrac{x^2 \sin^2 x}{[x^2 - (p\pi/2)^2][x^2 - (q\pi/2)^2]} & \text{if } p \text{ and } q \text{ are even} \\[3mm] \dfrac{x^2 \cos^2 x}{[x^2 - (p\pi/2)^2][x^2 - (q\pi/2)^2]} & \text{if } p \text{ and } q \text{ are odd} \\[3mm] 0 & \text{otherwise} \end{cases} \tag{4.5}$$

Alavi gives a related, though more complicated, formula for the $(\mathbf{ab}|\mathbf{cd})$ integrals themselves and then uses a three-dimensional discrete Fourier transform for their evaluation.[20]

In our second approach, we transform to intracule and extracule coordinates[26]

$$x = x_1 - x_2, \quad y = y_1 - y_2, \quad z = z_1 - z_2,$$
$$X = x_1 + x_2, \quad Y = y_1 + y_2, \quad Z = z_1 + z_2, \tag{4.6}$$

and integrate over the latter to reduce Eq. (4.2) to the three-dimensional integral

$$(\mathbf{p}|\mathbf{q}) = \frac{8}{\pi} \int_0^1 \int_0^1 \int_0^1 \frac{g_{p_x q_x}(x) g_{p_y q_y}(y) g_{p_z q_z}(z)}{\sqrt{x^2 + y^2 + z^2}} dx \, dy \, dz, \tag{4.7}$$

$$g_{pq}(x) = \begin{cases} 1 - x & \text{if } p = q = 0 \\[3mm] \dfrac{(1-x)\cos(p\pi x)}{2} - \dfrac{\sin(p\pi x)}{2p\pi} & \text{if } p = q > 0 \\[3mm] \dfrac{q\sin(q\pi x) - p\sin(p\pi x)}{(p^2 - q^2)\pi} & \text{if } |p - q| = 2,4,\ldots \\[3mm] 0 & \text{otherwise.} \end{cases} \tag{4.8}$$

We note that whereas the domain of the integral (4.4) is infinite that of (4.7) is finite.

In our third approach, we reduce both (4.4) and (4.7) to one-dimensional integrals, albeit with much more complicated integrands. Substituting the identity

$$\frac{1}{\sqrt{x^2 + y^2 + z^2}} \equiv \frac{2}{\sqrt{\pi}} \int_0^\infty \exp[-(x^2 + y^2 + z^2)u^2] du \tag{4.9}$$

into Eq. (4.7) and rearranging the order of integration yields

TABLE IV. A selection of low-order canonical $(\mathbf{p}|\mathbf{q})$ integrals [see Eq. (4.2) for definition] to ten-decimal places.

	$|000)$	$|002)$	$|022)$	$|222)$
$(000|$	+0.599 158 723 6			
$(002|$	−0.028 781 654 6	+0.032 796 910 6		
$(022|$	+0.002 382 563 8	−0.002 943 943 3	+0.008 052 393 7	
$(222|$	−0.000 226 945 7	+0.000 289 629 7	−0.000 650 719 2	+0.002 630 647 9
	$|001)$	$|003)$	$|023)$	$|223)$
$(001|$	+0.072 075 523 6			
$(003|$	−0.005 318 650 4	+0.016 988 706 2		
$(023|$	+0.000 590 143 3	−0.001 376 533 6	+0.005 488 646 1	
$(223|$	−0.000 063 446 9	+0.000 127 237 2	−0.000 393 930 2	+0.002 010 199 6
	$|011)$	$|013)$	$|033)$	$|233)$
$(011|$	+0.018 853 255 8			
$(013|$	−0.002 078 687 4	+0.006 801 120 3		
$(033|$	+0.000 298 761 7	−0.000 864 219 6	+0.004 180 006 7	
$(233|$	−0.000 029 661 2	+0.000 073 890 9	−0.000 270 556 2	+0.001 631 413 9
	$|111)$	$|113)$	$|133)$	$|333)$
$(111|$	+0.006 206 243 6			
$(113|$	−0.000 768 440 5	+0.002 817 002 5		
$(133|$	+0.000 109 537 4	−0.000 350 810 1	+0.001 840 075 6	
$(333|$	−0.000 016 284 8	+0.000 048 823 1	−0.000 208 085 6	+0.001 375 544 3

$$(\mathbf{p}|\mathbf{q}) = 2\int_0^\infty h_{p_x q_x}(u) p_{y q_y}(u) p_{p_z q_z}(u)\,du, \tag{4.10}$$

$$
h_{pq}(u) = \begin{cases}
\dfrac{\mathrm{erf}(u)}{u} + \dfrac{\exp(-u^2)-1}{u^2\sqrt{\pi}} & \text{if } p=q=0 \\[2ex]
\left(\dfrac{p\pi}{4u^2} - \dfrac{1}{2p\pi}\right)s_p(u) + \dfrac{c_p(u)}{2} + \dfrac{(-1)^p\exp(-u^2)-1}{2u^2\sqrt{\pi}} & \text{if } p=q>0 \\[2ex]
\dfrac{qs_q(u)-ps_p(u)}{(p^2-q^2)\pi} & \text{if } |p-q|=2,4,\ldots \\[2ex]
0 & \text{otherwise,}
\end{cases}
\tag{4.11}
$$

where the auxiliary functions $c_p(u)$ and $s_p(u)$ are the real and imaginary parts of

$$
\begin{aligned}
e_p(u) &= \frac{2}{\sqrt{\pi}}\int_0^1 \exp(ip\pi x)\exp(-u^2 x^2)\,dx \\
&= \frac{1}{u}\exp\left(-\frac{p^2\pi^2}{4u^2}\right)\left[\mathrm{erf}\left(u-\frac{ip\pi}{2u}\right) + \mathrm{erf}\left(\frac{ip\pi}{2u}\right)\right]
\end{aligned}
\tag{4.12}
$$

and $\mathrm{erf}(x)$ is the error function.[27] To our knowledge, the reduction of Coulomb integrals over particle-in-a-box functions to one-dimensional integrals has not previously been achieved.

The self-interaction energy is the simplest canonical and can be found in closed form

$$
\begin{aligned}
E_0 &= (000|000) \\
&= 2\int_0^\infty \left(\frac{\mathrm{erf}(u)}{u} + \frac{\exp(-u^2)-1}{u^2\sqrt{\pi}}\right)^3 du \\
&= \frac{2}{\pi}\ln(1+\sqrt{2})(2+\sqrt{3}) + \frac{2}{5\pi}(1+\sqrt{2}-2\sqrt{3}) - \frac{2}{3}.
\end{aligned}
\tag{4.13}
$$

Higher canonical integrals, a few of which are given in Table IV, are typically much smaller than E_0 but are more difficult to solve in closed form. We therefore chose to evaluate them by applying 320-point Gauss–Legendre quadrature[27] to each of the x, y, and z integrals in Eq. (4.7). We believe that all of our canonical integrals are accurate to at least ten decimal places.

TABLE V. Total energy E, Fock exchange energy E_K, Dirac exchange energy E_X, and HOMO-LUMO gap Δ for n electrons and N basis functions. Restricted Hartree–Fock (RHF) theory and a mean density $\langle\rho\rangle = 1$ e bohr^{-3} were used in all cases.

N	Configuration[a]		$N=26$	$N=60$	$N=87$	$N=133$	$N=178$
2	core(1)	E	17.144 16	17.144 15	17.144 15	17.144 15	17.144 15
		$-E_K$	2.402 34	2.402 37	2.402 37	2.402 37	2.402 37
		$-E_X$	2.080 17	2.080 24	2.080 24	2.080 24	2.080 24
		Δ	10.875	10.874	10.874	10.874	10.874
		$\langle\rho^2\rangle$	3.301	3.301	3.301	3.301	3.301
8	core(4)	E	48.041 28	48.039 05	48.038 63	48.038 50	48.038 49
		$-E_K$	7.866 72	7.865 57	7.864 41	7.864 20	7.864 22
		$-E_X$	7.342 65	7.342 01	7.340 56	7.340 40	7.340 43
		Δ	4.478	4.460	4.460	4.460	4.460
		$\langle\rho^2\rangle$	2.096	2.095	2.094	2.093	2.093
14	core(7)	E	74.624 02	74.491 74	74.488 15	74.484 64	74.484 45
		$-E_K$	13.468 44	13.342 99	13.335 94	13.329 05	13.328 86
		$-E_X$	12.510 91	12.432 25	12.425 46	12.417 58	12.417 48
		Δ	2.968	2.952	2.951	2.952	2.951
		$\langle\rho^2\rangle$	1.934	1.891	1.887	1.883	1.883
16	core(7)	E	84.951 99	84.704 43	84.699 08	84.695 49	84.694 65
	$+A_{1g}$	$-E_K$	15.026 24	14.876 66	14.869 07	14.861 81	14.860 80
		$-E_X$	14.157 72	14.053 64	14.046 23	14.038 59	14.037 34
		Δ	0.650	0.660	0.659	0.659	0.658
		$\langle\rho^2\rangle$	1.864	1.816	1.812	1.809	1.808
18	core(7)	E	93.328 53	93.002 38	92.993 30	92.987 90	92.984 47
	$+E_g$	$-E_K$	16.650 11	16.464 37	16.451 68	16.443 15	16.439 12
		$-E_X$	15.871 85	15.742 69	15.731 29	15.722 57	15.717 56
		Δ	0.779	0.791	0.791	0.790	0.790
		$\langle\rho^2\rangle$	1.832	1.780	1.776	1.772	1.770
20	core(10)	E	101.533 18	101.024 75	101.010 19	101.004 56	101.000 34
		$-E_K$	18.071 47	17.881 07	17.866 01	17.857 38	17.852 78
		$-E_X$	17.423 16	17.270 44	17.256 55	17.248 40	17.242 88
		Δ	0.427	0.473	0.473	0.471	0.471
		$\langle\rho^2\rangle$	1.751	1.698	1.693	1.690	1.688
22	core(11)	E	108.351 45	107.755 36	107.735 77	107.725 74	107.720 33
		$-E_K$	20.087 44	19.811 00	19.790 44	19.772 88	19.767 07
		$-E_X$	19.148 51	18.963 04	18.944 88	18.928 79	18.922 06
		Δ	2.120	2.146	2.147	2.145	2.145
		$\langle\rho^2\rangle$	1.756	1.697	1.691	1.685	1.683
28	core(11)	E	133.649 25	132.519 74	132.484 93	132.461 12	132.446 02
	$+T_{2u}$	$-E_K$	25.329 97	24.991 25	24.961 22	24.926 99	24.909 80
		$-E_X$	24.225 85	23.968 14	23.942 88	23.913 23	23.895 43
		Δ	0.860	0.766	0.764	0.764	0.765
		$\langle\rho^2\rangle$	1.723	1.662	1.656	1.648	1.644
34	core(17)	E	154.490 99	152.062 23	151.996 15	151.955 36	151.929 70
		$-E_K$	30.434 21	29.992 23	29.944 56	29.893 94	29.866 44
		$-E_X$	29.111 33	28.752 68	28.714 15	28.673 54	28.647 11
		Δ	1.578	1.714	1.693	1.691	1.690
		$\langle\rho^2\rangle$	1.655	1.591	1.583	1.575	1.570
40	core(20)	E	176.818 90	173.758 87	173.559 07	173.480 49	173.436 67
		$-E_K$	35.815 13	35.611 76	35.493 26	35.397 60	35.351 35
		$-E_X$	34.126 08	33.822 29	33.744 92	33.672 64	33.630 94
		Δ	1.738	1.701	1.660	1.665	1.665
		$\langle\rho^2\rangle$	1.640	1.601	1.588	1.575	1.568
46	core(23)	E	204.383 81	198.684 79	198.188 12	198.031 68	197.974 49
		$-E_K$	40.205 86	39.786 27	39.601 93	39.485 66	39.432 17
		$-E_X$	39.002 03	38.538 65	38.409 95	38.319 29	38.273 26
		Δ	0.165	0.478	0.447	0.458	0.455
		$\langle\rho^2\rangle$	1.597	1.543	1.525	1.512	1.505
48	core(23)	E	213.644 17	206.299 20	205.658 31	205.491 11	205.425 82
	$+A_{1g}$	$-E_K$	41.881 24	41.491 59	41.281 13	41.161 66	41.099 68
		$-E_X$	40.665 46	40.157 65	40.012 61	39.923 10	39.871 81

TABLE V.   (*Continued.*)

N	Configuration[a]		$N=26$	$N=60$	$N=87$	$N=133$	$N=178$
		Δ	−0.193	0.426	0.400	0.399	0.397
		$\langle\rho^2\rangle$	1.592	1.537	1.518	1.505	1.498
50	core(23)	E	219.701 96	213.084 24	212.232 26	212.057 70	211.980 97
	$+E_g$	$-E_K$	43.564 59	43.126 48	42.865 80	42.757 06	42.684 63
		$-E_X$	42.279 41	41.789 16	41.613 16	41.529 48	41.470 59
		Δ	0.808	0.540	0.531	0.538	0.537
		$\langle\rho^2\rangle$	1.582	1.530	1.508	1.497	1.489
52	core(26)	E	228.512 21	220.002 22	218.972 01	218.782 32	218.697 80
		$-E_K$	45.284 88	44.830 93	44.551 12	44.439 55	44.359 53
		$-E_X$	43.942 71	43.396 10	43.203 79	43.121 18	43.058 31
		Δ	No LUMO	1.147	1.162	1.176	1.177
		$\langle\rho^2\rangle$	1.577	1.523	1.500	1.490	1.482
58	core(26)	E	$\cdots$	242.635 36	241.499 51	240.985 36	240.861 94
	$+T_{1g}$	$-E_K$	$\cdots$	49.676 89	49.382 67	49.191 65	49.093 94
		$-E_X$	$\cdots$	48.293 30	48.093 53	47.951 32	47.874 55
		Δ	$\cdots$	0.546	0.448	0.498	0.500
		$\langle\rho^2\rangle$	$\cdots$	1.510	1.489	1.473	1.465
64	core(32)	E	$\cdots$	264.306 58	262.071 80	261.260 60	261.057 21
		$-E_K$	$\cdots$	54.524 97	54.225 57	53.941 24	53.808 44
		$-E_X$	$\cdots$	53.115 42	52.870 65	52.670 59	52.564 49
		Δ	$\cdots$	0.237	0.294	0.340	0.348
		$\langle\rho^2\rangle$	$\cdots$	1.491	1.469	1.449	1.439
70	core(35)	E	$\cdots$	282.251 75	279.202 38	278.364 60	278.127 81
		$-E_K$	$\cdots$	60.084 63	59.735 23	59.479 18	59.318 85
		$-E_X$	$\cdots$	58.048 54	57.772 92	57.594 21	57.477 11
		Δ	$\cdots$	0.792	0.958	0.967	0.967
		$\langle\rho^2\rangle$	$\cdots$	1.489	1.468	1.453	1.442
72	core(35)	E	$\cdots$	289.724 99	286.098 28	285.195 34	284.917 79
	$+A_{2u}$	$-E_K$	$\cdots$	61.948 28	61.570 19	61.298 86	61.116 91
		$-E_X$	$\cdots$	59.711 77	59.422 68	59.231 64	59.099 52
		Δ	$\cdots$	0.093	0.318	0.309	0.311
		$\langle\rho^2\rangle$	$\cdots$	1.490	1.469	1.453	1.442
74	core(35)	E	$\cdots$	295.486 47	292.246 29	291.254 41	290.950 56
	$+E_u$	$-E_K$	$\cdots$	63.698 15	63.337 05	63.006 52	62.817 01
		$-E_X$	$\cdots$	61.373 32	61.096 21	60.882 41	60.742 88
		Δ	$\cdots$	0.832	0.578	0.582	0.574
		$\langle\rho^2\rangle$	$\cdots$	1.491	1.472	1.454	1.442
76	core(38)	E	$\cdots$	302.520 41	298.715 50	297.663 88	297.309 27
		$-E_K$	$\cdots$	65.578 99	65.164 75	64.813 16	64.600 65
		$-E_X$	$\cdots$	63.031 26	62.735 81	62.509 05	62.352 57
		Δ	$\cdots$	0.964	1.130	1.058	1.085
		$\langle\rho^2\rangle$	$\cdots$	1.491	1.471	1.453	1.440
82	core(38)	E	$\cdots$	325.760 61	321.239 92	319.546 41	319.149 34
	$+T_{2u}$	$-E_K$	$\cdots$	70.212 59	69.942 84	69.501 26	69.298 15
		$-E_X$	$\cdots$	67.845 41	67.535 22	67.255 14	67.104 29
		Δ	$\cdots$	0.375	0.384	0.371	0.379
		$\langle\rho^2\rangle$	$\cdots$	1.477	1.459	1.438	1.427
88	core(44)	E	$\cdots$	348.801 06	342.165 29	339.801 96	339.362 20
		$-E_K$	$\cdots$	74.741 87	74.722 68	74.243 65	74.055 01
		$-E_X$	$\cdots$	72.525 91	72.274 48	71.957 50	71.817 17
		Δ	$\cdots$	0.138	0.338	0.305	0.312
		$\langle\rho^2\rangle$	$\cdots$	1.455	1.445	1.424	1.414
90	core(45)	E	$\cdots$	355.593 17	348.552 62	345.905 76	345.467 09
		$-E_K$	$\cdots$	76.498 95	76.521 26	76.055 82	75.870 70
		$-E_X$	$\cdots$	74.144 53	73.909 33	73.590 69	73.455 40
		Δ	$\cdots$	0.435	0.810	0.835	0.837
		$\langle\rho^2\rangle$	$\cdots$	1.453	1.445	1.425	1.416
92	core(45)	E	$\cdots$	364.573 52	356.568 66	353.704 24	353.100 81
	$+A_{1g}$	$-E_K$	$\cdots$	77.952 33	77.858 63	77.407 19	77.195 40
		$-E_X$	$\cdots$	75.758 58	75.478 82	75.146 05	74.994 52

TABLE V.   (*Continued.*)

N	Configuration[a]		$N=26$	$N=60$	$N=87$	$N=133$	$N=178$
		Δ	$\cdots$	-0.388	0.032	0.036	0.111
		$\langle \rho^2 \rangle$	$\cdots$	1.450	1.439	1.419	1.409
94	core(45)	E	$\cdots$	373.377 19	364.108 77	361.108 24	360.417 97
	$+E_g$	$-E_K$	$\cdots$	79.099 85	79.145 86	78.696 61	78.467 82
		$-E_X$	$\cdots$	77.274 67	77.038 79	76.692 01	76.526 79
		Δ	$\cdots$	-0.423	0.090	0.066	0.126
		$\langle \rho^2 \rangle$	$\cdots$	1.440	1.433	1.412	1.402
96	core(48)	E	$\cdots$	382.312 48	371.828 71	368.606 87	367.718 12
		$-E_K$	$\cdots$	80.507 59	80.448 13	80.013 95	79.765 64
		$-E_X$	$\cdots$	78.872 57	78.594 61	78.233 35	78.051 55
		Δ	$\cdots$	-0.546	-0.011	-0.021	0.072
		$\langle \rho^2 \rangle$	$\cdots$	1.436	1.427	1.406	1.395
102	core(48)	E	$\cdots$	402.106 65	391.143 13	387.215 05	386.310 69
	$+T_{1g}$	$-E_K$	$\cdots$	85.676 94	85.877 45	85.337 70	85.105 32
		$-E_X$	$\cdots$	83.738 88	83.512 36	83.109 13	82.937 88
		Δ	$\cdots$	0.036	0.193	0.094	0.169
		$\langle \rho^2 \rangle$	$\cdots$	1.433	1.428	1.407	1.397
108	core(54)	E	$\cdots$	424.315 98	410.383 07	405.052 19	404.058 54
		$-E_K$	$\cdots$	90.617 60	91.083 77	90.642 32	90.412 80
		$-E_X$	$\cdots$	88.560 64	88.348 58	87.941 47	87.769 66
		Δ	$\cdots$	0.477	0.731	0.728	0.771
		$\langle \rho^2 \rangle$	$\cdots$	1.425	1.424	1.405	1.396
114	core(54)	E	$\cdots$	449.041 62	431.744 08	425.364 90	424.057 87
	$+T_{2u}$	$-E_K$	$\cdots$	95.433 94	95.715 08	95.322 21	95.009 31
		$-E_X$	$\cdots$	93.456 76	93.171 88	92.730 21	92.509 38
		Δ	$\cdots$	0.569	0.526	0.473	0.447
		$\langle \rho^2 \rangle$	$\cdots$	1.423	1.418	1.399	1.388
120	core(60)	E	$\cdots$	474.855 49	452.413 85	444.665 33	442.901 19
		$-E_K$	$\cdots$	100.512 67	100.316 26	99.999 68	99.594 70
		$-E_X$	$\cdots$	98.335 19	97.931 66	97.453 81	97.177 94
		Δ	$\cdots$	No LUMO	0.737	0.722	0.752
		$\langle \rho^2 \rangle$	$\cdots$	1.419	1.409	1.390	1.377
126	core(63)	E	$\cdots$	$\cdots$	473.900 94	464.751 06	462.731 68
		$-E_K$	$\cdots$	$\cdots$	105.642 18	105.199 92	104.685 66
		$-E_X$	$\cdots$	$\cdots$	102.852 98	102.352 30	102.024 27
		Δ	$\cdots$	$\cdots$	0.362	0.360	0.364
		$\langle \rho^2 \rangle$	$\cdots$	$\cdots$	1.411	1.392	1.377
132	core(66)	E	$\cdots$	$\cdots$	496.188 77	484.930 16	482.197 85
		$-E_K$	$\cdots$	$\cdots$	110.176 74	109.909 59	109.329 84
		$-E_X$	$\cdots$	$\cdots$	107.559 20	107.074 36	106.696 78
		Δ	$\cdots$	$\cdots$	0.078	0.160	0.238
		$\langle \rho^2 \rangle$	$\cdots$	$\cdots$	1.401	1.385	1.368
138	core(69)	E	$\cdots$	$\cdots$	515.696 47	502.595 61	499.625 55
		$-E_K$	$\cdots$	$\cdots$	115.127 80	115.126 56	114.559 50
		$-E_X$	$\cdots$	$\cdots$	112.288 26	111.867 25	111.504 41
		Δ	$\cdots$	$\cdots$	0.282	0.645	0.666
		$\langle \rho^2 \rangle$	$\cdots$	$\cdots$	1.393	1.383	1.368
140	core(69)	E	$\cdots$	$\cdots$	522.692 10	509.315 47	506.187 61
	$+A_{2g}$	$-E_K$	$\cdots$	$\cdots$	116.668 71	116.693 82	116.112 54
		$-E_X$	$\cdots$	$\cdots$	113.881 23	113.452 80	113.080 27
		Δ	$\cdots$	$\cdots$	0.287	0.345	0.313
		$\langle \rho^2 \rangle$	$\cdots$	$\cdots$	1.392	1.381	1.366
142	core(69)	E	$\cdots$	$\cdots$	530.984 81	516.258 05	512.861 51
	$+E_g$	$-E_K$	$\cdots$	$\cdots$	118.138 59	118.262 27	117.676 56
		$-E_X$	$\cdots$	$\cdots$	115.467 46	115.015 56	114.644 46
		Δ	$\cdots$	$\cdots$	-0.056	0.258	0.255
		$\langle \rho^2 \rangle$	$\cdots$	$\cdots$	1.390	1.379	1.364
144	core(69)	E	$\cdots$	$\cdots$	537.820 18	522.752 55	519.198 01
	$+A_{2g}+E_g$	$-E_K$	$\cdots$	$\cdots$	119.661 21	119.814 87	119.215 66
		$-E_X$	$\cdots$	$\cdots$	117.052 01	116.593 64	116.209 02

TABLE V.   (*Continued.*)

N	Configuration[a]		N=26	N=60	N=87	N=133	N=178
		Δ	⋯	⋯	−0.062	0.264	0.258
		$\langle\rho^2\rangle$	⋯	⋯	1.388	1.376	1.362
146	core(69)	E	⋯	⋯	546.254 55	529.793 59	525.749 08
	$+A_{1g}+A_{2g}+E_g$	$-E_K$	⋯	⋯	121.122 91	121.374 68	120.766 63
		$-E_X$	⋯	⋯	118.611 75	118.164 37	117.767 82
		Δ	⋯	⋯	−0.591	0.014	0.142
		$\langle\rho^2\rangle$	⋯	⋯	1.384	1.374	1.360
148	core(69)	E	⋯	⋯	554.296 32	536.533 08	532.046 79
	$+A_{2g}+2E_g$	$-E_K$	⋯	⋯	122.411 34	122.802 17	122.238 39
		$-E_X$	⋯	⋯	120.144 49	119.732 18	119.324 45
		Δ	⋯	⋯	−0.553	0.048	0.161
		$\langle\rho^2\rangle$	⋯	⋯	1.380	1.372	1.357
150	core(75)	E	⋯	⋯	563.082 98	543.421 23	538.405 08
		$-E_K$	⋯	⋯	123.790 32	124.332 43	123.767 26
		$-E_X$	⋯	⋯	121.670 13	121.296 41	120.872 24
		Δ	⋯	⋯	−0.899	−0.035	0.105
		$\langle\rho^2\rangle$	⋯	⋯	1.375	1.370	1.355
152	core(75)	E	⋯	⋯	571.104 61	549.575 89	544.397 29
	$+A_{2u}$	$-E_K$	⋯	⋯	125.447 80	126.063 42	125.500 50
		$-E_X$	⋯	⋯	123.270 68	122.890 31	122.458 96
		Δ	⋯	⋯	−0.979	−0.045	0.102
		$\langle\rho^2\rangle$	⋯	⋯	1.374	1.369	1.354
154	core(75)	E	⋯	⋯	575.336 29	555.197 30	549.737 00
	$+E_u$	$-E_K$	⋯	⋯	127.262 69	127.890 16	127.260 94
		$-E_X$	⋯	⋯	124.889 14	124.526 06	124.078 04
		Δ	⋯	⋯	−0.231	0.078	0.258
		$\langle\rho^2\rangle$	⋯	⋯	1.374	1.370	1.354
156	core(78)	E	⋯	⋯	583.183 72	561.132 12	555.516 44
		$-E_K$	⋯	⋯	128.935 40	129.646 79	129.007 50
		$-E_X$	⋯	⋯	126.489 02	126.120 69	125.664 32
		Δ	⋯	⋯	−0.274	0.326	0.576
		$\langle\rho^2\rangle$	⋯	⋯	1.373	1.369	1.354
162	core(78)	E	⋯	⋯	604.822 54	579.867 42	574.170 65
	$+T_{2u}$	$-E_K$	⋯	⋯	134.067 31	134.775 27	134.167 23
		$-E_X$	⋯	⋯	131.287 84	130.932 67	130.499 75
		Δ	⋯	⋯	0.240	0.551	0.412
		$\langle\rho^2\rangle$	⋯	⋯	1.370	1.368	1.354
168	core(78)	E	⋯	⋯	630.068 74	598.915 80	592.241 90
	$+T_{1u}+T_{2u}$	$-E_K$	⋯	⋯	139.100 82	140.034 76	139.403 01
		$-E_X$	⋯	⋯	136.098 36	135.759 34	135.309 65
		Δ	⋯	⋯	0.902	0.751	0.790
		$\langle\rho^2\rangle$	⋯	⋯	1.367	1.367	1.354
174	core(87)	E	⋯	⋯	662.205 29	621.090 99	613.637 63
		$-E_K$	⋯	⋯	143.712 84	143.966 98	143.341 33
		$-E_X$	⋯	⋯	140.948 45	140.437 07	139.931 56
		Δ	⋯	⋯	No LUMO	0.086	0.100
		$\langle\rho^2\rangle$	⋯	⋯	1.365	1.360	1.346

[a]The notation "core(k)" means the first k basis functions listed in Table II.

V. RESULTS AND DISCUSSION

Our program can handle arbitrary values of n, N, and $\langle\rho\rangle$ but, in the interests of brevity, we present data here only for a selection of 45 electron numbers n, five basis set sizes N, and $\langle\rho\rangle=1$. In each case, Table V shows the total energy E, the Fock exchange energy E_K, the Dirac exchange energy E_X, the HOMO-LUMO gap Δ, and the mean square density $\langle\rho^2\rangle$.

The five basis sets consist of all of the functions in Table II with energies $m^2 \leq 20$, 30, 40, 50, or 60 and are of size $N=26$, 60, 87, 133, and 178, respectively. By examining the rows of Table V, one can quickly discern the extent to which the tabulated properties have converged with increasing basis set size.

The total energy of a cube of *uniform* electron density with a uniform background charge is an intensive property and scales exactly linearly with the volume of the cube. According to Thomas–Fermi–Dirac (TFD) theory,[1] the total energy per electron when $\langle\rho\rangle=1$ is the Thomas–Fermi kinetic
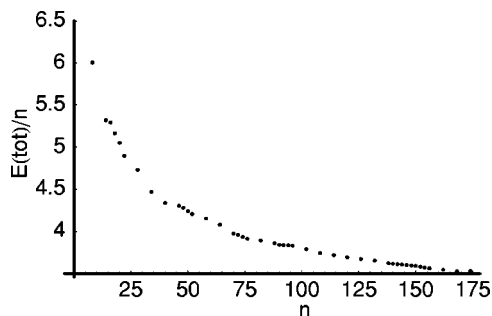
FIG. 1. Total energy for n electrons (mean density $\langle\rho\rangle=1$ e bohr^{-3}) in a cube. RHF theory with $N=178$ basis functions was used.
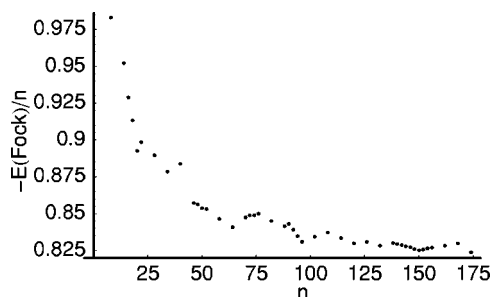

FIG. 3. Dirac exchange energy for n electrons (mean density $\langle\rho\rangle$ $=1$ e bohr^{-3}) in a cube. RHF theory with $N=178$ basis functions was used.

coefficient C_F minus the Dirac exchange coefficient C_X, that is,

$$\lim_{n\to\infty}(E/n) = \frac{3}{10}(3\pi^2)^{2/3} - \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} = 2.132\,675\ldots\,. \tag{5.1}$$

However, because the electron density in a finite jellium system vanishes on the faces of the cube, it is clear that $\rho(\mathbf{r})$ cannot be uniform. As a result, when n is finite, E/n is larger than expected and, even for $n=174$ electrons, exceeds the asymptotic value by 50% (Fig. 1).

The Fock exchange energy[28] for an electronic system is given by

$$E_K = -\frac{1}{4}\sum_{\mathbf{abcd}} P_{\mathbf{ab}}P_{\mathbf{cd}}(\mathbf{ad}|\mathbf{bc}) \tag{5.2}$$

and we know from TFD theory that, for a uniform electron gas with $\langle\rho\rangle=1$,

$$\lim_{n\to\infty}(-E_K/n) = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} = 0.738\,558\ldots\,. \tag{5.3}$$

Although we would not expect $-E_K/n$ to match this value exactly in finite jellium systems, Fig. 2 shows that the difference is only 12% for $n=174$ electrons, indicating that E_K/n approaches its asymptotic value much more rapidly than E/n and suggesting that exchange effects in finite jellia are short ranged. This is reasonable when we recall that the exchange intracule[29] $K(u)$ for jellium decays as u^{-6}.

The Dirac exchange energy[6,7] is given by
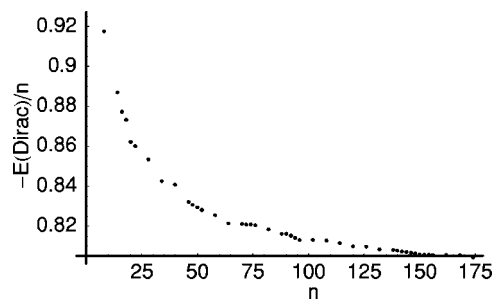
$$E_X = -C_X\int\rho(\mathbf{r})^{4/3}d\mathbf{r}, \tag{5.4}$$

where $\rho(\mathbf{r})$ is the density. Equations (5.2) and (5.4) yield identical energies (by construction) when applied to infinite jellium but give different results elsewhere. The Dirac integral for a finite jellium system,

$$\int\rho(\mathbf{r})^{4/3}d\mathbf{r} = \int_0^\pi\int_0^\pi\int_0^\pi\left(\sum_{\mathbf{ab}}P_{\mathbf{ab}}\phi_{\mathbf{a}}(\mathbf{r})\phi_{\mathbf{b}}(\mathbf{r})\right)^{4/3}dx\,dy\,dz, \tag{5.5}$$

cannot be evaluated in closed form and we have resorted instead to 50-point Gauss–Legendre quadrature[27] for each of the three integrals in Eq. (5.5). We expect $-E_X/n$, like $-E_K/n$, to approach C_X as n becomes large, and Fig. 3 confirms that this is the case. In fact, $-E_X/n$ is only 9% greater than C_X for $n=174$ electrons and appears to converge both more quickly and more smoothly than the analogous Fock ratio.

The nonuniformity of an electron density is quantified by its variance

$$\mathrm{Var}[\rho] = \langle(\rho-\langle\rho\rangle)^2\rangle = \langle\rho^2\rangle - \langle\rho\rangle^2 \tag{5.6}$$

and, since $\langle\rho\rangle=1$ in all cases considered here, the nonuniformity of our densities is given simply by the deviation of $\langle\rho^2\rangle$ from unity. Figure 4 shows that $\langle\rho^2\rangle$ decays fairly smoothly as n increases but that the density is still significantly nonuniform ($\mathrm{Var}[\rho]\approx0.35$) even when the number of electrons has risen to $n=174$.

The magnitude of the energy gap between HOMO and LUMO provides a simple measure of the conductivity of the system and has interesting connections with electron corre-
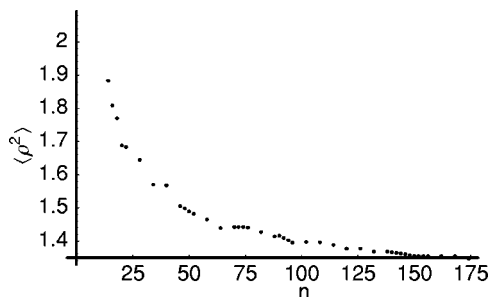

FIG. 2. Fock exchange energy for n electrons (mean density $\langle\rho\rangle$ $=1$ e bohr^{-3}) in a cube. RHF theory with $N=178$ basis functions was used.

FIG. 4. Mean square density for n electrons (mean density $\langle\rho\rangle=1$ e bohr^{-3}) in a cube. RHF theory with $N=178$ basis functions was used.
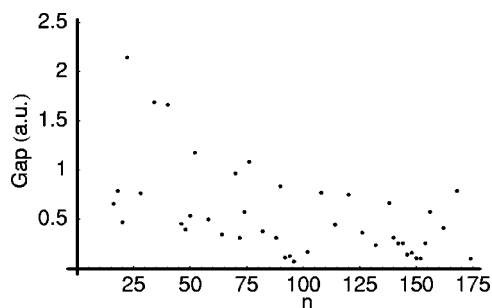
FIG. 5. HOMO-LUMO gap for n electrons (mean density $\langle\rho\rangle=1$ e bohr^{-3}) in a cube. RHF theory with $N=178$ basis functions was used.

lation effects and wave function stability.[30–32] Since there is no band gap in infinite jellium, one would expect the HOMO-LUMO gap in finite jellia to tend to zero as n tends to infinity. This seems to be supported by Fig. 5 but the convergence is erratic and surprisingly hard systems (in the Pearson–Parr sense[1]) appear even when n is quite large: the gap of roughly 0.8 a.u. (21 eV) in the case of 168 electrons is a particularly impressive example. However, it should be noted that Hartree–Fock theory is well known to exaggerate band gaps (because the energy of the LUMO arises from interactions with all n electrons and is therefore spuriously high) and one can predict with confidence that Kohn–Sham calculations, for example, would yield much smaller HOMO-LUMO gaps.

Choosing the coefficient C_X to ensure that E_K and E_X are equal in infinite jellium leads to the value in Eq. (5.3). However, it was discovered long ago that slightly larger values yield better results in finite systems and Slater's X_a model[33] was built on this empirical foundation. By considering the ratio between Eqs. (5.2) and (5.4), we have calculated

$$C_X = \frac{\sum_{\mathbf{abcd}}P_{\mathbf{ab}}P_{\mathbf{cd}}(\mathbf{ad}|\mathbf{bc})}{4\int\rho(\mathbf{r})^{4/3}d\mathbf{r}} \tag{5.7}$$

for each of our finite jellium systems and Fig. 6 shows these coefficients as a function of n. Their behavior is erratic and they remain significantly larger than the Dirac constant in Eq. (5.3) even in the largest systems that we have studied. Although the coefficient will presumably converge toward the Dirac value as n tends to infinity, it appears that n must be very large before this becomes an accurate approximation.
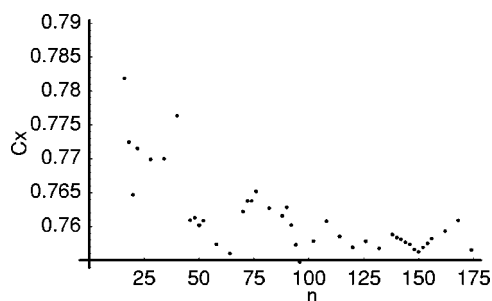

FIG. 6. The C_X ratio (5.7) for n electrons (mean density $\langle\rho\rangle=1$ e bohr^{-3}) in a cube. RHF theory with $N=178$ basis functions was used.

VI. CONCLUDING REMARKS

In this paper, we have used restricted Hartree–Fock theory to examine the energies and properties of n electrons, with unit mean density, confined to a cube. We have considered 45 particular values of n lying between 2 and 174 and, in each case, we have expanded the RHF orbitals in a basis set with up to 178 particle-in-a-box functions (viz., all those with $m^2 \leqslant 60$). We observe that, as n increases, the total energy and exchange energy per particle converge smoothly toward their limiting values, but the HOMO-LUMO gap and Dirac coefficient converge erratically. In all cases, the convergence is slow.

We are currently extending this work in several directions. First, we are developing closed-form expressions for the general canonical integral (4.2). Possession of compact formulas for these will enable us to employ larger basis sets in future studies. Second, we are devising accurate methods for extrapolating our finite-n results toward the $n=\infty$ limit. This will enable us to predict the properties of large but finite ensembles of electrons. Third, we have discovered that many of our RHF wave functions possess triplet instabilities[30–32] and we are therefore now exploring symmetry-broken solutions to the corresponding (unrestricted) Hartree–Fock equations. We will report these and other results elsewhere.

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