

Temperature-Dependent Behavior of Confined Many-electron Systems in the Hartree-Fock Approximation

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Many-electron systems at substantial finite temperatures and densities present a major challenge to density functional theory. Very little is known about the free-energy behavior over the temperature range of interest, for example, in the study of warm dense matter. As a result, it is difficult to assess the validity of proposed approximate free-energy density functionals. Here we address, at least in part, this need for detailed results on well-characterized systems for purposes of testing and calibration of proposed approximate functionals. We present results on a comparatively simple, well-defined, but computationally feasible model, namely thermally occupied Hartree-Fock states for eight one-electron atoms at arbitrary positions in a hard-walled box. We discuss the main technical tasks (defining a suitable basis and evaluation of the required matrix elements) and discuss the physics which emerges from the calculations.

I. INTRODUCTION

Warm dense matter (WDM) is encountered in systems as diverse as the interiors of giant planets^{1,2} and in the pathway to inertial confinement fusion^{3,4}. WDM is challenging to theory and simulation because it occurs inconveniently, for theory, between the comparatively well-studied plasma and condensed matter regimes. Both the Coulomb coupling parameter $\Gamma := Q^2/(r_s k_B T)$ and electron degeneracy parameter $\Theta := k_B T/\varepsilon_F$ are approximately unity for WDM. (Q = relevant charge, r_s = Wigner radius, ε_F = electron Fermi energy, T = temperature, k_B = Boltzmann constant.) A non-perturbative treatment therefore is required.

Contemporary computations on WDM^{5–18} are dominated by use of the Kohn-Sham (KS) realization of thermal density functional theory (DFT)^{19–25} to generate a potential surface for ionic motion (treated classically). The great majority of these calculations use approximate ground-state exchange-correlation (XC) functionals, E_{xc} , with the XC temperature dependence picked up implicitly from the T-dependence of the density $n(\mathbf{r}, T)$. Though fruitful, this approach is not without potential difficulties, as is illustrated in Fig. 3 of Ref. 7. Two difficulties are germane here.

First, nothing is known about the implicit T-dependence of ground-state approximate E_{xc} functionals, whether they be constraint-based or empirical. Compared to the ground-state situation, there is only a small literature on explicitly T-dependent functionals, that is, XC free energy functionals, and essentially all of those studies are at the level of the local-density approximation^{26–42}.

Second is the technical problem of solving for the Kohn-Sham orbitals and eigenvalues. Since the computational load from the eigenvalue problem scales, in general, as order N_{orbitals}^3 , the growth in the number of non-negligibly occupied KS orbitals with increasing temperature is a clear computational bottleneck. See the re-

marks, for example, in Sec. 4 of Ref. 18. For complicated systems, the same bottleneck is encountered in ground-state simulations which use the DFT Born-Oppenheimer energy surface to drive the ionic dynamics. One result has been the emergence of active research on orbital-free DFT (OFDFT), that is, approximate functionals for the ingredients of the KS free energy, namely the KS kinetic energy (KE) \mathcal{T}_s , entropy \mathcal{S}_s , and XC free energy \mathcal{F}_{xc} or their ground-state counterparts. Almost all of this effort has been for ground-state OFKE functionals^{43–46}. With OFDFT functionals in hand, the DFT extremum condition yields a single non-linear Euler equation for the density which supplants the KS equation for the orbitals. (Note that most of the OFKE literature invokes the KS separation of the KE in order to use existing E_{xc} approximations consistently.) The finite-temperature OFDFT work is dominated by variants on Thomas-Fermi-von Weizsäcker theory; see for example Ref. 41 and references therein. That type of theory, however, is known (on both fundamental and computational grounds) to be no more than qualitatively accurate in many circumstances.

Little or nothing is known about the accuracy of approximate OFDFT functionals at finite temperature and there is little fiduciary data for comparison. The aim of the present study is to provide such data for the combination of a well-defined physical system and a well-defined methodology.

II. SYSTEM AND METHODOLOGY

We shall treat a neutral system of N_{ion} (here $N_{ion} \leq 8$ for computational convenience) one-electron atoms with nuclei fixed at arbitrary positions in a hard-walled three-dimensional rectangular box. The confined system allows systematic treatment of pressure effects at stipulated finite temperature, hence is a small, treatable sample of WDM. Note the corresponding use of a small number of atoms in Ref. 18. Also note the considerable literature on

spherically confined systems at $T = 0$ K^{47–52}. We have not found any work on lower symmetry confinement of multi-atom systems at non-zero T . At non-zero T there is a large literature on average-atom methods, for example Refs. 18,53 and many others, but such methods do not provide the fiduciary data needed for functional development.

As a many-electron problem, a clearly defined approximation is required. We choose the finite temperature Hartree-Fock (FTHF) scheme^{54–56}, with issues of electron correlation to be addressed in the future. In addition to being well-defined, FTHF provides the advantage that its $T = 0$ K limit is the *lingua franca* of molecular electronic structure interpretation. Use of FTHF therefore also provides at least a semi-quantitative framework for understanding chemical processes in WDM.

The FTHF Euler equations to be solved (in unrestricted form) are

$$\begin{aligned} \varepsilon_i \varphi_i(\mathbf{r}) = & \left(-\frac{1}{2} \nabla^2 + U_{ion}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) \\ & + \sum_j f_j \int d\mathbf{r}' \frac{|\varphi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \varphi_i(\mathbf{r}) \\ & - \sum_j \delta_{\sigma_i \sigma_j} f_j \int d\mathbf{r}' \frac{\varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \varphi_j(\mathbf{r}), \quad (1) \end{aligned}$$

with U_{ion} the ion-electron interaction potential and σ_i the spin label; the sums are over all spin orbitals. Unless indicated otherwise we use hartree atomic units ($\hbar = m_e = e = 1$; energy is then in hartrees, 1 hartree = 27.2116 eV, and lengths are in bohrs, 1 bohr = 0.52918 angstrom). The spin orbitals (eigenstates, φ_i) have Fermi-Dirac thermal occupations

$$f_i = \left(1 + e^{\beta(\varepsilon_i - \mu)} \right)^{-1}, \quad N = \sum_i f_i, \quad (2)$$

where $\beta = 1/k_B T$ and μ is the electron chemical potential. These equations, along with specification of the nuclear sites and imposition of hard-wall boundary conditions, completely describe the problem. The free energy and entropy are given by

$$\mathcal{F} = \sum_i f_i \varepsilon_i - \frac{1}{2} \sum_{i,j} f_i f_j (J_{i,j} - K_{i,j}) - TS, \quad (3)$$

$$\mathcal{S} = \sum_i f_i \ln(f_i) + (1 - f_i) \ln(1 - f_i), \quad (4)$$

with conventional definitions of J and K :

$$J_{i,j} := \int d\mathbf{r} d\mathbf{r}' \frac{|\varphi_i(\mathbf{r})|^2 |\varphi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (5)$$

$$K_{i,j} := \delta_{\sigma_i \sigma_j} \int d\mathbf{r} d\mathbf{r}' \frac{\varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_i^*(\mathbf{r}') \varphi_j^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (6)$$

Note that, so far, we have implemented only the restricted Hartree-Fock approximation (RHF; non-spin-polarized in DFT language; closed-shell or spin-compensated in quantum chemistry language).

A. Gaussian Basis Calculations

The Gaussian-type-orbital (GTO) basis methods first introduced by Boys^{61–65} are widely exploited in modern computational codes for molecular systems. Boundary conditions for free molecules, namely that the orbitals vanish at infinity, are satisfied automatically by a GTO basis. For a hard-wall confined system, the basis functions must vanish at the boundary, so standard molecular GTO matrix-element expressions are inapplicable. This fact illustrates the most critical technical issue for the calculation, namely, to find a basis that both satisfies the boundary conditions yet allows for an efficient enough evaluation of the two-electron integrals to be computationally tractable on reasonable resources. A second, closely related technical issue is that the high temperature also dictates what is “efficient enough”, in that the basis must be large enough and flexible enough to represent a sufficient number of thermally occupied higher-energy orbitals of the system, hence to represent the density and free energy accurately.

Those considerations eliminate several seemingly plausible options for a basis. For example, a real-space finite-difference/element scheme, while suitable for a DFT calculation or a Hartree-Fock calculation on a free diatomic molecule (for which curvilinear coordinates can be exploited⁵⁷), is far too expensive for the present case because of the number of matrix elements to be calculated. Another example is sine functions. They also satisfy the boundary condition, but an adequate description of the rapidly varying electronic distribution near the nuclei requires prohibitively many matrix elements in our multi-center problems. So we chose an adaptation of standard GTO methods which uses modified Gaussians that meet the boundary condition, yet retain enough efficiency to complete the calculation.

The various ways in which a GTO can be forced to zero at the bounding planes of a rectangular box can have great impact upon the efficiency of the matrix element calculations. Compared with familiar practice for free molecules, in general the confined case requires more primitive GTOs for each contracted one. More importantly, the finite integration volume makes it impossible to achieve completely analytic calculation of the two-electron integrals, which is, of course, precisely the category in which computational efficiency is most needed. We have addressed this issue by using truncated Gaussians as described in the next section.

B. Truncated Gaussians

The rectangular box makes Cartesian GTOs a convenient choice, because each primitive function is then separable into Cartesian factors which are simple 1D functions. Consider the Cartesian factor

$$g^n(x) = (x - x_c)^n e^{-\alpha(x-x_c)^2} \quad (7)$$

To force this function to zero at the box boundaries $x = 0$ and $x = L_x$, we subtract a constant equal to the function value at each end. When x_c is not at the box center, the value to be subtracted differs for the two ends, so we split the function into two pieces, make the two subtractions, and scale the two pieces such that the resulting function is continuous. Each unnormalized Cartesian factor becomes

$$\begin{aligned} g_{box}^n(x) &= a_0 (g^n(x) - \Delta_0) & 0 \leq x \leq x_c \\ &= a_L (g^n(x) - \Delta_{L_x}) & x_c \leq x \leq L_x \end{aligned} \quad (8)$$

with $\Delta_0 = g^n(0)$, $\Delta_{L_x} = g^n(L_x)$. We call this the truncated GTO (tGTO) basis.

Two technical issues remain. The tGTO functions may not have continuous derivatives, so proper evaluation of the kinetic energy matrix elements requires attention. Appendix A shows that nothing untoward happens and that the kinetic energy is simply a sum of piecewise contributions, except for p -type functions which have a simple correction term. Second is the matter of evaluating two-electron matrix elements. In Appendix B, we show that this task reduces to computing finite-range integrals of products of Gaussians and error functions. At this juncture, we are doing those via Gauss-Legendre quadrature. We also note that the tGTO basis is simpler than the smoothly cut-off floating spherical GTO basis of Ref. 51 in the sense that their cut-off introduces a mixing of two symmetry types (*e.g.* s, d) in each basis function.

III. RESULTS AND DISCUSSION

A. Zero Temperature

Two simple ground-state test cases, the H atom and the H₂ molecule, illustrate the system behavior with increasing confinement (decreasing volume) as well as the correctness of our implementation. The confined-system energies should be above the ground-state energies (in the basis selected) of the corresponding free systems and approach those free-system energies (and bond length for the molecule) in the limit of large box volume.

For the hydrogen atom in the center of a cubical box, Fig. 1 (a) shows the ground-state energy for confinements $L \leq 10$ bohr. The basis is shown in Table I and described in the next section. The calculations were carried out to $L = 30$ bohr. Beyond 10 bohr there was negligible difference in the energy with respect to the free-atom energy

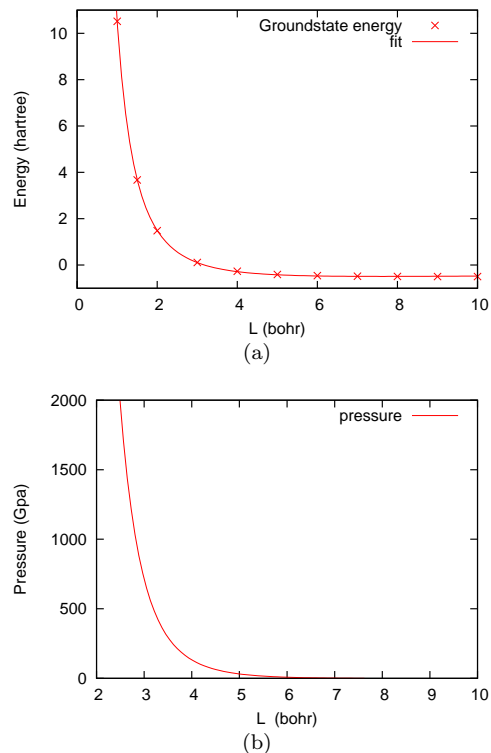


FIG. 1: (a) Ground-state energy of an H atom in the center of a cube with edge length L . Fit is for function $f(L) = a/L^2 + b/L + c$. (b) Pressure calculated from the energy fit.

in the same basis, precisely as expected. At $L = 30$ bohr the ground-state energy is identical with the free-atom GTO calculation using the same basis, namely -0.498476 hartree, validating our overlap, kinetic, and nuclear energy integral calculations. A fit to the energies as a function of cube edge L

$$E(L) = a/L^2 + b/L + c, \quad 0 \leq L \leq 10 \text{ bohr} \quad (9)$$

yields $a = 14.5733$ hartree bohr², $b = -3.82369$, hartree bohr, $c = -0.238258$ hartree. Though this fit does not have the correct infinite-size limit, it is the best fit of this simple form for $0 \leq L \leq 10$ bohr. From this fit the pressure, $p = -dE/dV$ ($V = L^3$) can be calculated; see Fig. 1 (b).

The effects of spherical versus cubic confinement can be assessed easily by comparison of the two confinement types both for bounding volumes and equal volumes. For bounding volumes, the circumscribed-sphere $R = \sqrt{3}L/2$ and inscribed-sphere $R = L/2$ results from⁵⁹ (also see⁵⁸) can be compared to our cube results. Figure 2 shows that the energy of the cubically confined system is bounded by that of the two spherical systems, as would be expected. Shape effects of confinement are shown in Fig. 3. Though the spherical system has a lower energy than that of the equal volume cubical system, they are quite close until the cube is smaller than $L \approx 4$ bohr, where a significant indication of shape dependence begins. At $L = 1$ bohr

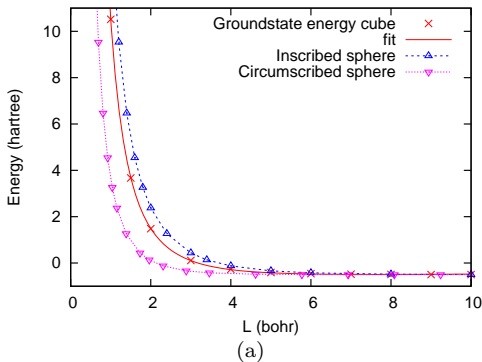


FIG. 2: Comparison of ground-state energy of an H atom in a cube with its energy within two bounding spheres.

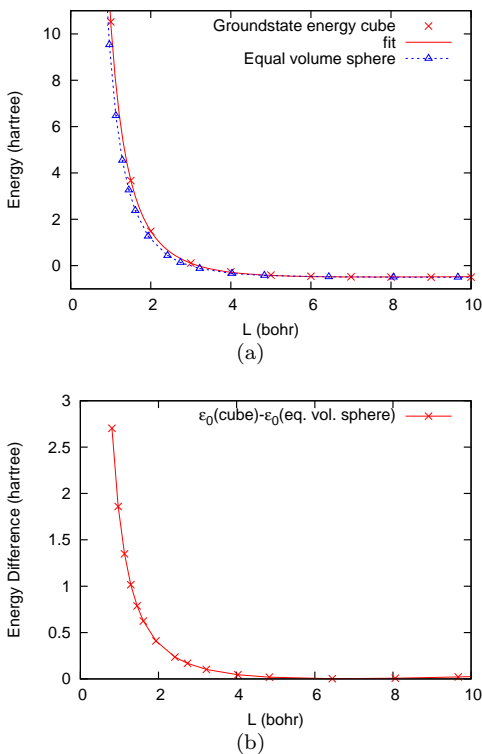


FIG. 3: (a) Comparison of energy of an H atom in a cube with that in a sphere of equal volume. (b) The difference of the two ground-state energies.

the difference in energy is over 25%, as shown in Fig. 3 (b). A simpler basis of six s -type tGTO with exponents $[0.15, 0.3, 0.6, 1.2, 2.4, 4.8 \text{ bohr}^{-2}]$ reproduces the ground-state energies for $L \geq 1.5 \text{ bohr}$.

Next consider the confined H_2 molecule at zero temperature. Here we used the simpler six-tGTO basis just given. For a large cube, the new tGTO confined-box computations again should conform to known results for the integrals and produce essentially the energy vs. bond length curve for the free molecule. With $L = 30 \text{ bohr}$ and the molecule centered in the cube and aligned along

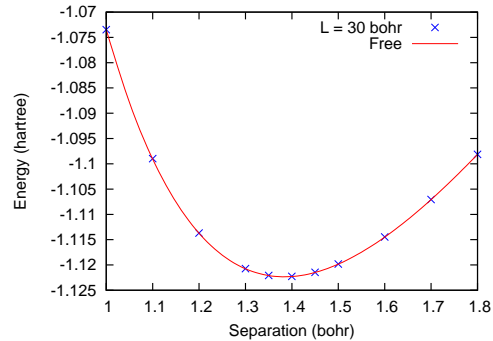


FIG. 4: Energy versus atomic separation for the H_2 molecule centered in a 30 bohr cube. The ground-state agrees exactly with the free GTO calculation using the same primitives as a basis.

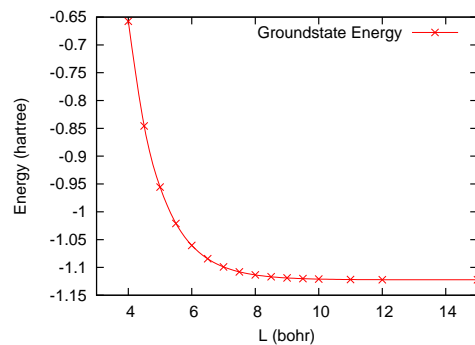


FIG. 5: Ground-state energy for H_2 with bond length 1.4 bohr confined in cube of edge length L .

the body diagonal, we get energies shown as points in Fig. 4. These agree completely with the values of the free GTO calculation, which are shown in that figure as the $E(R)$ curve. The minimum is at 1.383 bohr, satisfactorily close to the free-molecule RHF value of 1.385 bohr from a 6-31G** basis calculation⁶⁰. Conversely for fixed R (at 1.4 bohr) and decreasing L (to 4 bohr), the ground-state energy behavior is shown in Fig. 5. The onset of confinement effects becomes visible in the vicinity of $L \approx 11 \text{ bohr}$. Optimization of the bond length R at $L = 5 \text{ bohr}$ is shown in Fig. 6. The total energy is, of course, higher than for the larger box, and the optimal R is shifted down to 1.178 bohr from 1.383 bohr.

Following this method, we obtain the optimized R and energy for decreasing L . A function fit to the energy similar to that used earlier yields R as a function of the pressure, as shown in Fig. 7.

B. Finite Temperature

For finite-temperature calculations, at least a single p orbital needs to be included, and as many orbitals as feasible should be available to represent the fractionally occupied levels which become increasingly important as

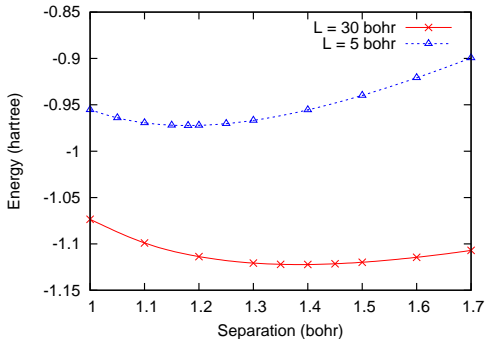


FIG. 6: Energy vs. bond length for the H_2 molecule centered in cubes $L = 30$ and $L = 5$ bohr. The minima are at 1.383 and 1.178 bohr respectively.

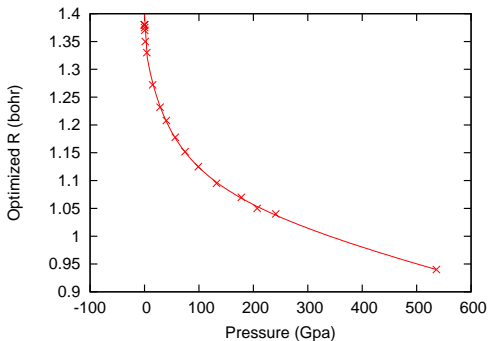


FIG. 7: Optimized bond length, R , for the H_2 molecule vs. pressure.

T is increased. For all the following calculations, except where noted, the basis consists of seven s -type primitive GTOs and one p_x , one p_y , and one p_z GTO, with the p -GTO exponents equal. An elementary exponent optimization was done as follows. A set of five s -type exponents was picked and held fixed: $[0.1, 0.2, 0.4, 0.8, 1.6 \text{ bohr}^{-2}]$. The sixth exponent was optimized to minimize ε_{1s} for the single atom centered in a cube of specified L . With those six exponents fixed, the seventh s -GTO exponent was used to minimize ε_{2s} . With those seven fixed, the p exponent was used to minimize ε_{2p} . Additionally, for small L the smallest exponents produce orbitals that are so similarly flat that an approximate linear dependence exists and diagonalization fails. When this happens the smallest exponent is replaced by extending the even-tempered exponent series to larger values. For example at $L = 4$ the 0.1 exponent is replaced with 3.2, at $L = 2$ the 0.2 exponent is also replaced with 6.4.

This procedure keeps the ratio of the effective length ($1/\sqrt{\alpha}$) of the most diffuse function to the edge length L at 0.75-0.79 for $L \leq 3$, with smaller ratios for larger L .

The optimization was done for each L . Table I shows the resulting exponents and energies for the orbitals that were optimized.

With this volume-dependent optimized basis, calculations were done for a single atom at the center of a cube

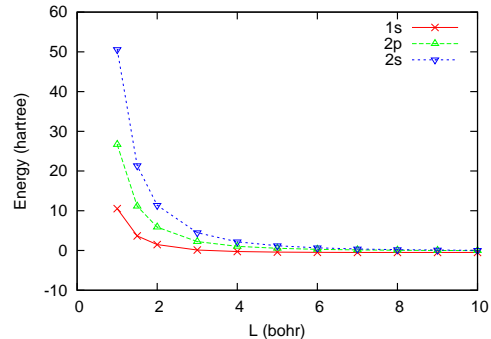


FIG. 8: Lowest five eigenstate energies of H as a function of cube edge L . Energy values are from Table I.

with $1 \leq L \leq 15$ bohr. The orbital energies of the five lowest states ($1s, 2p_x, 2p_y, 2p_z, 2s$) are plotted in Fig. 8. Notice the inversion of ordering ($2p$ below $2s$) that is a result primarily of the confinement. To address finite temperature for this single-electron system, the one-electron levels were populated according to the Fermi-Dirac distribution. Observe that the one-electron Hamiltonian is independent of density, so the one-electron orbitals and eigenenergies are independent of occupancy, even though the density and total electronic energy are not. The left-hand panel in Fig. 9 shows the resulting total energy as a function of L for four values of T , while the right-hand panel shows the free energy. The weak minimum in total energy in the vicinity of 6 bohr at $T=50$ kK appears to be a confinement effect. We have found a similar minimum at about the same volume by doing a Fermi-Dirac population of the high-precision eigenvalues of the spherically confined H atom given in Ref. 59.

Figure 10 shows the contributions to the free energy for the single atom as a function of T for four cube volumes ($L = 2, 3, 7, 15$ bohr). At $L = 7$ bohr, the KE is flat with T at almost its $T = 0$ K value. The $T = 50$ kK nuclear-electron attraction E_{Ne} , however, is much stronger for $L = 7$ bohr than for $L = 15$ bohr. By $L = 3$ bohr, the KE and E_{Ne} are roughly equal in magnitude.

Figure 10 also shows that the KE for the $L = 15$ bohr system falls with increasing temperature. Though this might seem odd, it is as it should be from virial theorem arguments for the free atom. The $2s$ KE is one-fourth the $1s$ value⁶⁶. Finite temperature population of the $2s$ and depopulation of the $1s$ therefore reduces the KE with respect to its $T = 0$ K value.

Next we turn to the system of eight H atoms. We examined a symmetric configuration in which the eight atoms were situated at the corners of a smaller cube, edge-length $L/2$, centered within the hard-wall cube, edge-length L . The basis used was ten s -type GTOs centered on each atom. Strict s -type symmetry is broken, of course, by enforcement of the hard-wall boundary conditions. An even-tempered set of exponents also was used in this case: $[0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, 25.2, 50.4, 100.8 \text{ bohr}^{-2}]$. As a test, the calculations were redone with two

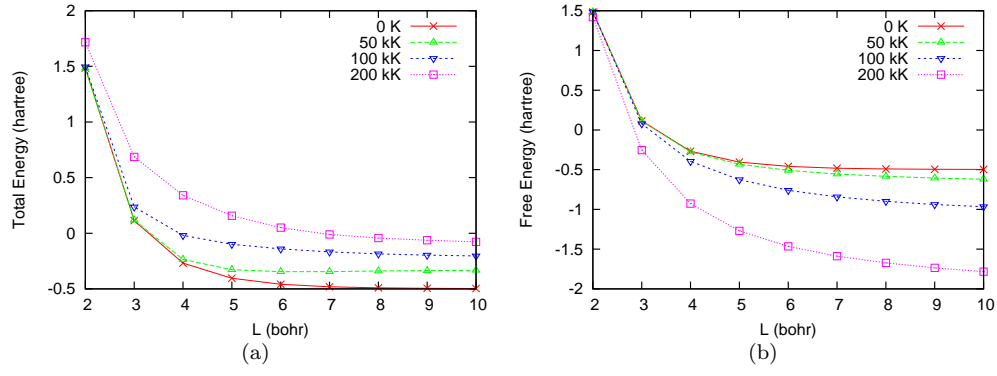


FIG. 9: (a) Single H atom total energy, $E = \mathcal{F} + TS$, and (b) free energy, \mathcal{F} as a function of cube edge L , with the one-electron levels populated according to the Fermi distribution.

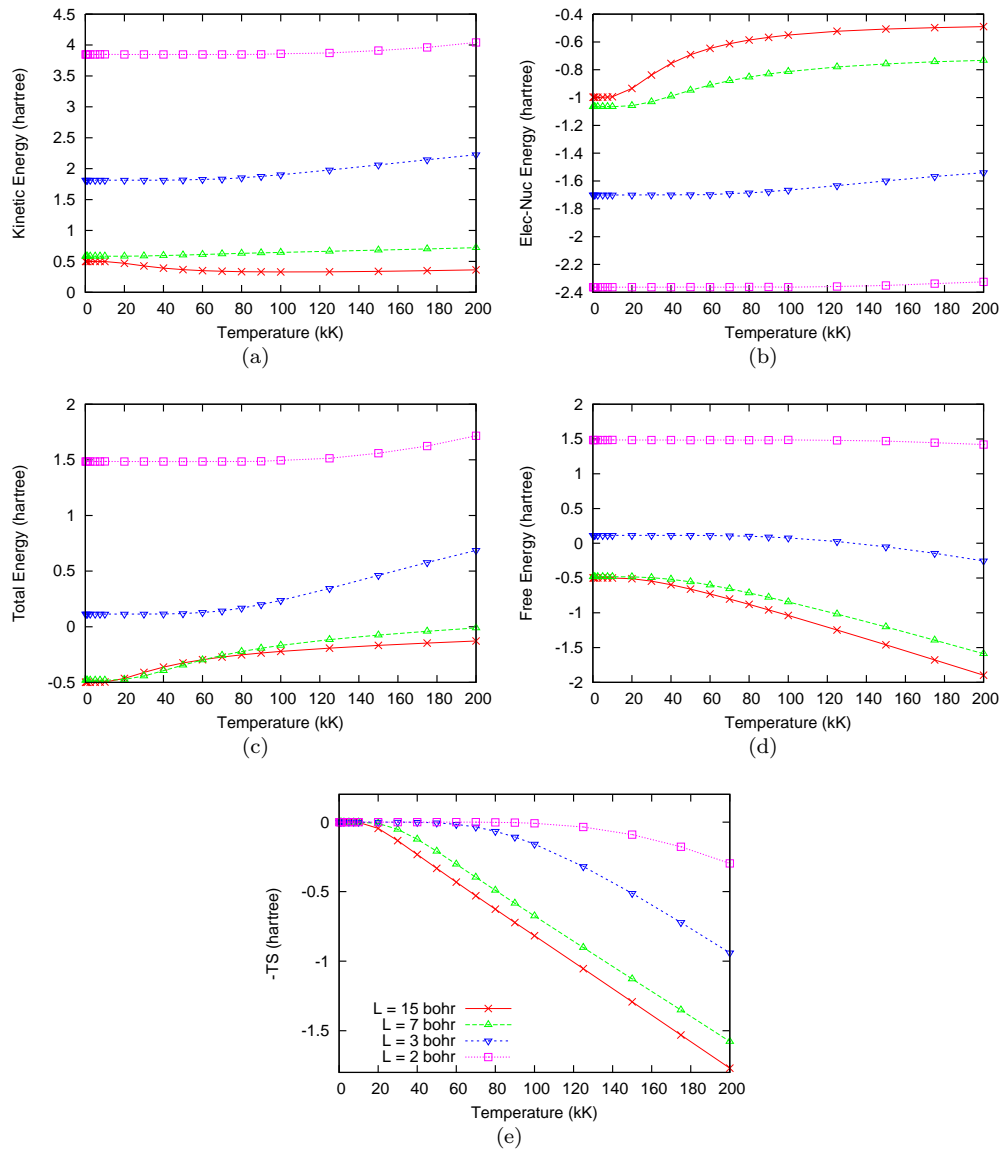


FIG. 10: Energy components of a cubically confined single H atom vs. temperature. (a) kinetic energy, (b) electron-nuclear energy, (c) total energy, (d) free energy, (e) entropic energy [(d)-(c)]. Key for all is shown in (e).

L	fixed	1s	2s	2p	ϵ_{1s}	ϵ_{2s}	ϵ_{2p}
1.0	1.6, 3.2, 6.4, 12.8, 25.6	179.1	244 (NA)	4.01	10.518	50.5898	26.683
1.5	0.8, 1.6, 3.2, 6.4, 12.8	92.15	244 (NA)	1.88	3.6738	21.3545	11.154
2	0.4, 0.8, 1.6, 3.4, 6.8	48	250	1.115	1.48471	11.3649	5.8753
3	0.2, 0.4, 0.8, 1.6, 3.4	24.5	175	0.545	0.11385	4.47073	2.25356
4	0.2, 0.4, 0.8, 1.6, 3.4	21.2	7.0	0.34	-0.268848	2.18313	1.06314
5	0.1, 0.2, 0.4, 0.8, 1.6	11.2	3.7	0.235	-0.40474	1.18372	0.547955
6	"	10.4	2.5	0.18	-0.458898	0.675591	0.288794
7	"	17.7	2.25	0.15	-0.481704	0.389716	0.145105
8	"	10.2	0.195	0.122	-0.491112	0.217062	0.0591604
9	"	10.2	0.07	0.103	-0.495291	0.10651	0.00450443
10	"	10.2	0.0365	0.088	-0.497104	0.0327616	-0.0321549
11	"	10.1	0.023	0.076	-0.497889	-0.0179536	-0.0578267
12	"	10.1	0.018	0.0665	-0.498227	-0.0535872	-0.0764093
13	"	10.1	0.015	0.059	-0.498372	-0.0789901	-0.0901715
14	"	10.05	0.014	0.053	-0.498435	-0.0972631	-0.100500
15	"	10.1	0.014	0.048	-0.498461	-0.108291	-0.108291

TABLE I: Optimized exponents and orbital energies for an H atom at the center of a cube of edge length L . $2p$ refers to the triply degenerate p_x , p_y , and p_z states. For $L < 2$, the $2s$ level could not be optimized beyond the first 6 exponents.

fewer basis functions per atom; the exponents [50.4,100.8 bohr⁻²] were removed. The two calculations agreed to 2 millihartree in total and component energies up to 200 kK. Matrix elements are calculated only once and stored, after which fully self-consistent calculations may be done at many temperatures.

Figure 11 shows the total energy $E = \mathcal{F} + TS$ as a function of L for various temperatures, as well as the free energy \mathcal{F} itself. The nuclear-nuclear repulsion energy is included. Though constant with respect to temperature, it varies with L . Figure 12 shows various components of the free energy (electron-nuclear Coulomb energy, electron-electron Coulomb energy including exchange, kinetic energy, and entropic energy). Also shown are the total energy and free energy, with the difference of these two being the entropic energy. Again, nuclear-nuclear repulsion energy is included in these two plots. It has values of 9.118, 7.598, 5.699, 4.559 hartree for $L = 5, 6, 8, 10$ bohr, respectively. The energies are shown as a function of temperature $0 \leq T \leq 250$ kK for four cube sizes, $L = 5, 6, 8,$ and 10 bohr. The comparatively flat plateau up to roughly $T = 15$ kK is a direct consequence of Fermi-Dirac level filling. Up to about 25 kK, the interval between the highest occupied molecular orbital (HOMO) at zero temperature and the lowest unoccupied molecular orbital (LUMO) is roughly constant at 0.5 hartree. Therefore the filling ratio of those two is roughly $\exp(-13/1.3) \approx 5 \times 10^{-5}$ or smaller up to about $T = 15$ kK. We return to this matter shortly.

It is well known that zero-temperature HF calculations over-estimate band gaps in solids and so-called HOMO-LUMO gaps of finite systems. This happens because the occupied HF orbitals are free of self-interaction, whereas the unoccupied ones are not. In the FTHF scheme however, as temperature increases, levels unoccupied at $T = 0$ K become increasingly fractionally occupied (as well as shifted). In the self-consistent solution of the HF problem

in a basis, those levels then contribute to the Hamiltonian matrix (“Fock matrix” in quantum chemistry terminology). To address the extent to which FTHF exhibits HOMO-LUMO gap over-estimation as does ground-state HF and at what degree of fractional occupancy an energy level is changed from an overestimated virtual to a properly estimated partially occupied one, we consider the eigenspectrum of a single, moderately compressed eight-atom cube with $L = 6$ bohr.

Figure 13 shows the Fermi distribution of the single-particle energies for four temperatures. The continuous curve is the Fermi function with calculated chemical potential μ , and the points are the input energies to the calculation of μ . Then in Fig. 14, μ is plotted as a function of T . At $T = 0$, the fourth and fifth energy levels, ϵ_4 and ϵ_5 , are the HOMO and LUMO respectively. One can see that the spacing between them decreases with temperature. This difference is shown directly in Fig. 15 along with the occupation number for the ϵ_5 level. Observe also in Fig. 14 that the chemical potential is nearly exactly halfway between these levels. This behavior, which is exact at zero temperature, actually holds to just below 50 kK. It is of note that the $\epsilon_2, \epsilon_3, \epsilon_4$ levels are degenerate in energy, as are the next three levels $\epsilon_5, \epsilon_6, \epsilon_7$.

Those total energy and eigenspectrum results together resolve the matter of the behavior of what would be virtual states at zero temperature in FTHF. First, examination of the kinetic and total energy plots for all box sizes shows that there is a change in the form of the temperature dependence at roughly 20 kK. That change is complemented by the change in the spacing between the ϵ_4 and ϵ_5 levels. They are essentially static for lower temperatures, then begin to change abruptly well below 50 kK, and then change more moderately at higher temperatures. Thus, above 50 kK, states corresponding to zero-temperature virtuals are sufficiently incorporated in

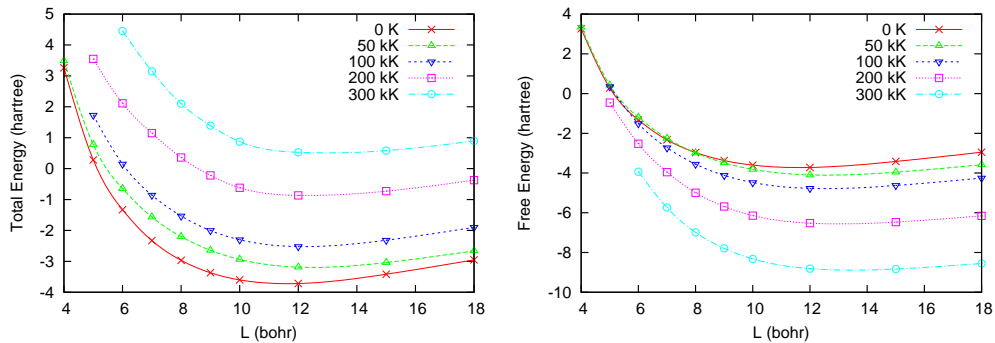


FIG. 11: Zero and finite-temperature total energy and free energy for eight H atoms in different sized cubes: (a) $E = \mathcal{F} + TS$, (b) \mathcal{F} .

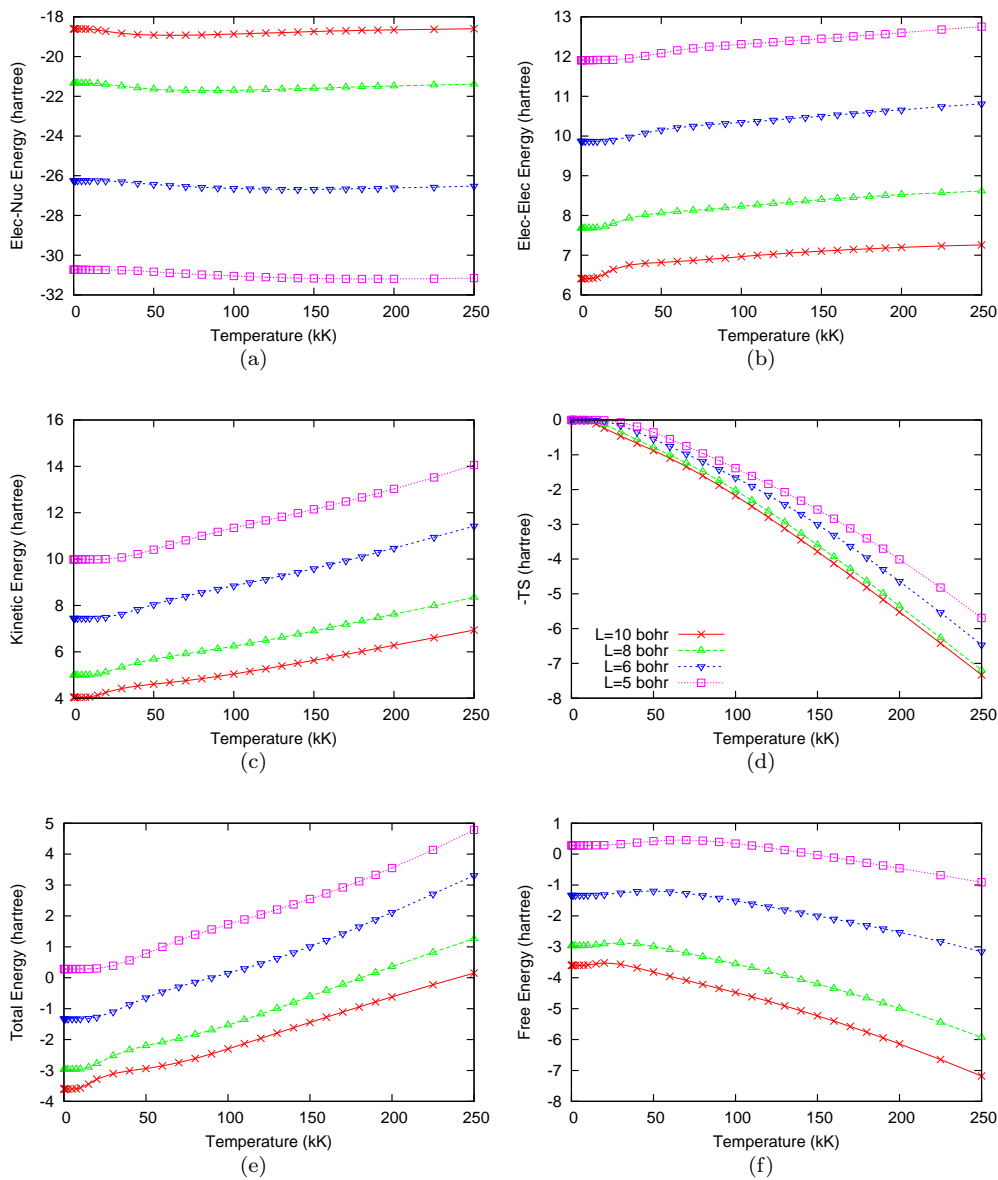


FIG. 12: Self-consistent FTHF free energy contributions for eight confined H atoms in a cubic array as a function of T for four different cube edge lengths L . Key for all is given in (d).

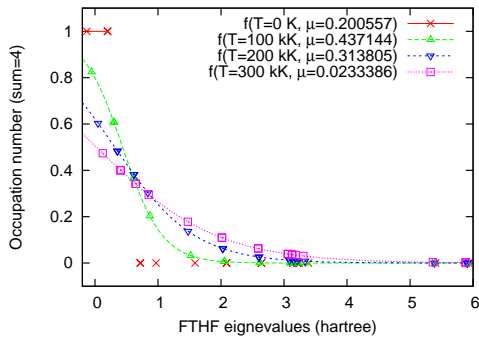


FIG. 13: Fermi distribution for eight H atoms in a box of size $L = 6$ bohr. Points may represent more than one state due to energy degeneracies.

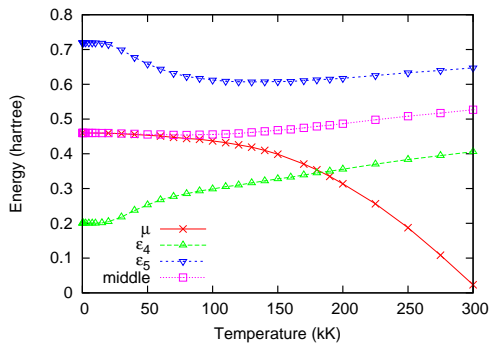


FIG. 14: Chemical potential and the fourth and fifth energy levels. The curve labeled “middle” is half way between ε_4 and ε_5 .

the interaction terms to make a material modification of $T = 0$ behavior. However, as the temperature is decreased below roughly 50 kK, the FTHF Coulomb and exchange terms increasingly are dominated by the $T = 0$ occupied levels, which therefore keeps the lightly occupied higher energy levels artificially high. This is not a basis issue, but an issue with discrete eigenstates. In a solid such as jellium or a metal with a continuum of states, this should not be an issue, but for a system with energy gaps the issue remains.

C. Computational cost

For these calculations, the cost is essentially entirely in the cpu time for the calculation of the two-electron integrals. The eight-atom systems described are calculated with 64 or 80 total basis functions, making diagonalization trivial. A simple double array of all N^4 two-electron integrals only occupies 128 or 312.5 MB respectively, storable in memory. In practice we calculated N^4/λ integrals, with $\lambda = 7.60, 7.68$ and not 8 due to the looping procedure we used. While for the cubic system discussed here, this calculation requirement could have been reduced further by exploiting symmetry, we need

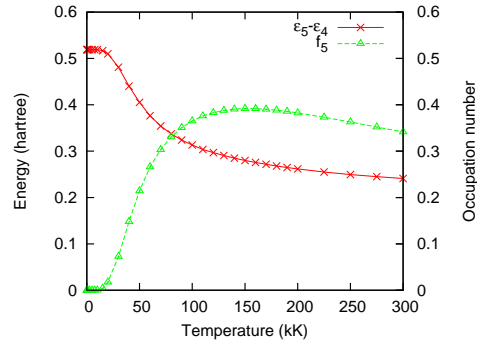


FIG. 15: Energy difference between the fourth and fifth energy levels along with the occupation number of the fifth energy level.

the capability to explore other, lower symmetry geometries. Note however that if the box size or the atomic positions are changed, all integrals affected by the change will need to be recalculated.

On a modern desktop processor (Intel Core i5 650 at 3.2 Ghz) one two-electron integral can be calculated in about 29.1 ms. So the times to calculate all integrals for a 64- or 80-orbital basis would be 17.84 hr and 43.13 hr. The integrals are calculated independently, so can be parallelized effectively. Calculations reported in this work were done on the University of Florida High Performance Computing Center Linux clusters.

IV. ACKNOWLEDGEMENT

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Appendix A: Correction for Piecewise Integrals for the Basis Functions

From the definition of the basis functions in Eqs. (7) and (8), it follows that derivatives of the basis function may not be continuous at x_c , the center of the function. A discontinuity of the second derivative would, of course, be significant for the kinetic energy. The issue is whether the kinetic energy matrix elements can be evaluated piecewise, as is the case with the overlap, nuclear-electron, and electron-electron integrals. We may examine this issue by writing the basis formally with Heaviside functions, as follows:

$$\varphi = [\theta(x) - \theta(x - x_1)] \varphi_0 + [\theta(x - x_1) - \theta(x - L)] \varphi_L \quad (\text{A1})$$

For the tGTO basis, the identification from Eq. 8 is

$$\begin{aligned}\varphi_0 &= a_0 (g^n(x) - \delta_0) \\ \varphi_L &= a_L (g^n(x) - \delta_L) \\ g^n(x) &= (x - x_1)^n e^{-\alpha(x-x_1)^2}, \quad x_1 = x_c\end{aligned}\quad (\text{A2})$$

The derivatives are

$$\begin{aligned}\frac{\partial \varphi}{\partial x} &= [\delta(x) - \delta(x - x_1)] \varphi_0 + [\theta(x) - \theta(x - x_1)] \varphi'_0 \\ &\quad + [\delta(x - x_1) - \delta(x - L)] \varphi_L \\ &\quad + [\theta(x - x_1) - \theta(x - L)] \varphi'_L\end{aligned}\quad (\text{A3})$$

and

$$\begin{aligned}\frac{\partial^2 \varphi}{\partial x^2} &= [\delta'(x) - \delta'(x - x_1)] \varphi_0 + 2 [\delta(x) - \delta(x - x_1)] \varphi'_0 \\ &\quad + [\theta(x) - \theta(x - x_1)] \varphi''_0 \\ &\quad + [\delta'(x - x_1) - \delta'(x - L)] \varphi_L \\ &\quad + 2 [\delta(x - x_1) - \delta(x - L)] \varphi'_L \\ &\quad + [\theta(x - x_1) - \theta(x - L)] \varphi''_L\end{aligned}\quad (\text{A4})$$

Now consider a generic kinetic energy matrix element involving the foregoing function and another, similar basis function χ with left and right constituents χ_0, χ_L , centered at x_2 . Without loss of generality, take $x_1 < x_2$. Then

$$\int_0^L \chi \frac{\partial^2 \varphi}{\partial x^2} dx := I_A + I_B \quad (\text{A5})$$

$$\begin{aligned}I_B &= \chi_0 (\varphi'_L - \varphi'_0) \Big|_{x=x_1} - \int \delta(x - x_1) (\varphi_L - \varphi_0) [[\delta(x) - \delta(x - x_1)] \chi_0 + [\theta(x) - \theta(x - x_1)] \chi'_0 \\ &\quad + [\delta(x - x_1) - \delta(x - L)] \chi_L + [\theta(x - x_1) - \theta(x - L)] \chi'_L] dx\end{aligned}\quad (\text{A9})$$

Note χ_0 in the first term follows because the functions themselves are continuous, while the first and second derivatives may not be. For the same reason, it follows that the remaining integral in Eq. (A9) and the second term of Eq. (A8) vanish. Thus so long as the functions are continuous, the correction to the piecewise kinetic energy integral is simply

$$I_B = \chi (\varphi'_L - \varphi'_0) \Big|_{x=x_1} \quad (\text{A10})$$

and so long as the first derivative is continuous, this reduces to zero.

With continuity of the basis functions enforced by construction, only the first derivative needs to be examined for a possible correction to simple piecewise integration.

The terms of the second derivative with the Heaviside functions contribute just the piecewise integration I_A , while the delta function and first derivative delta function terms contribute I_B . Of the terms in Eq. A4 only those at x_1 contribute, as the constituents $\chi_0, \chi_L, \varphi_0$, and φ_L go to zero at $x = 0$ and $x = L$. Thus

$$\begin{aligned}I_B &= \int \chi_0 [\delta'(x - x_1) (\varphi_L - \varphi_0) \\ &\quad + 2\delta(x - x_1) (\varphi'_L - \varphi'_0)] dx.\end{aligned}\quad (\text{A6})$$

From the definition of δ' this expression becomes

$$\begin{aligned}I_B &= \int \chi_0 [-\delta(x - x_1) (\varphi'_L - \varphi'_0) \\ &\quad + 2\delta(x - x_1) (\varphi'_L - \varphi'_0)] - \chi'_0 \delta(x - x_1) (\varphi_L - \varphi_0) dx\end{aligned}\quad (\text{A7})$$

which reduces to

$$I_B = [\chi_0 (\varphi'_L - \varphi'_0) - \chi'_0 (\varphi_L - \varphi_0)] \Big|_{x=x_1} \quad (\text{A8})$$

For the case of $x_1 = x_2$, that is, for diagonal terms or functions that have the same center, χ'_0 must be replaced in Eq. (A7) by the analog of Eq. (A3), with the result

For the basis defined in Eqs. (8), those corrections are

$$\begin{aligned}g^0(x) &= e^{-\alpha(x-x_1)^2} & I_B &= 0 \\ g^1(x) &= (x - x_1) e^{-\alpha(x-x_1)^2} & I_B &= \chi(a_L - a_0) \\ g^2(x) &= (x - x_1)^2 e^{-\alpha(x-x_1)^2} & I_B &= 0\end{aligned}\quad (\text{A11})$$

Basis functions $g^n(x)$ with higher powers of the prefactor $(x - x_1)$ all have continuous first and second derivatives at x_1 . In fact, those derivatives are all zero. So only the p -type basis functions, ($n = 1$), have a kinetic energy matrix element contribution beyond that given by piecewise integration.

Appendix B: Finite-Range Gaussian Integrals

Following the methods of Boys^{61–65} we use the transform of the Coulomb potential to separate the Coulomb integrals into one-dimensional Cartesian pieces:

$$\begin{aligned} \frac{1}{|\mathbf{r} - \mathbf{R}_N|} &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-s^2(\mathbf{r} - \mathbf{R}_N)^2} ds \\ &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-s^2(x - X_N)^2} e^{-s^2(y - Y_N)^2} e^{-s^2(z - Z_N)^2} ds. \end{aligned} \quad (\text{B1})$$

Hence all Coulomb integrals require integration over the transform variable s , which is done by Gauss-Laguerre quadrature.

For 1D primitive tGTOs, we note the following finite range (a, b) integrals. First the primitive s-type gaussian is given as

$$g(x) = e^{-\alpha(x-x_c)^2} \quad (\text{B2})$$

The basic integral is then

$$\begin{aligned} I_0 &= \int_a^b e^{-\alpha(x-x_c)^2} dx \\ &= \int_{a-x_c}^{b-x_c} e^{-\alpha x'^2} dx' \\ &= \frac{\sqrt{\pi}}{2\sqrt{\alpha}} \operatorname{erf}(\sqrt{\alpha}x') \Big|_{a-x_c}^{b-x_c} \end{aligned} \quad (\text{B3})$$

Next consider a prefactor of x :

$$\begin{aligned} I_1 &= \int_a^b x e^{-\alpha(x-x_c)^2} dx \\ &= \int_{a-x_c}^{b-x_c} (x' + x_c) e^{-\alpha x'^2} dx' \\ &= -\frac{e^{-\alpha x'^2}}{2\alpha} \Big|_{a-x_c}^{b-x_c} + x_c I_0 \end{aligned} \quad (\text{B4})$$

For the x^2 term we consider the derivative of the basic integral,

$$\begin{aligned} \int_{a-x_c}^{b-x_c} x'^2 e^{-\alpha x'^2} dx' &= -\frac{dI_0}{d\alpha} \\ &= \left[\frac{\sqrt{\pi}}{4\alpha^{3/2}} \operatorname{erf}(\sqrt{\alpha}x') - \frac{x'}{2\alpha} e^{-\alpha x'^2} \right] \Big|_{a-x_c}^{b-x_c} \\ &= \frac{1}{2\alpha} I_0 - x' \frac{e^{-\alpha x'^2}}{2\alpha} \Big|_{a-x_c}^{b-x_c} \end{aligned} \quad (\text{B5})$$

This result leads to

$$\begin{aligned} I_2 &= \int_a^b x^2 e^{-\alpha(x-x_c)^2} dx \\ &= \int_{a-x_c}^{b-x_c} (x' + x_c)^2 e^{-\alpha x'^2} dx' \\ &= \frac{1}{2\alpha} I_0 - x' \frac{e^{-\alpha x'^2}}{2\alpha} \Big|_{a-x_c}^{b-x_c} - \frac{x_c e^{-\alpha x'^2}}{\alpha} \Big|_{a-x_c}^{b-x_c} + x_c^2 I_0 \end{aligned} \quad (\text{B6})$$

For inclusion of tGTO functions up to p -type, we continued this procedure through I_4 . All two-center (overlap, nuclear-electron, kinetic) integrals reduce to expressions in terms of I_n . Four-center (two-electron) integrals, after applying the gaussian product rule twice, reduce to

$$\int_{a_2}^{b_2} \int_{a_1}^{b_1} e^{-\alpha_1(x_1-x_i)^2} e^{-\alpha_2(x_2-x_j)^2} e^{-s^2(x_1-x_2)^2} dx_1 dx_2 \quad (\text{B7})$$

After two more applications of the product rule we may perform one integral as I_0 and arrive at

$$\int_{a_2}^{b_2} \operatorname{erf}(a(b-x_2)) e^{-c(x_2-d)^2} dx_2 \Big|_{x_1=a_1}^{x_1=b_1} \quad (\text{B8})$$

which we evaluate by Gauss-Legendre quadrature.

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