Semiclassical Ground-State Energies of Many-Electron Systems

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A new semiclassical method is proposed to obtain accurate ground-state energies for many-electron systems. The method borrows its semiclassical character from Thomas-Fermi (TF) theory, but improves upon it by including exchange-correlation effects, at least approximately. We illustrate our method (correlated TF method) on simple models of 1D-interacting electrons, showing that it yields dramatic improvements over TF theory, particularly in the strongly correlated regime.

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Determining accurate ground-state energies of matter at all levels of aggregation has remained one of the major challenges of computational chemistry and physics for the past 80 years. Solving numerically the N-electron Schrödinger equation is implausible for systems containing more than a few electrons, but ingenious ideas have been developed to find approximate solutions (Ref. [1] presents a good overview from a quantum-chemistry viewpoint).

In the midst of recent resurgent interest in the semiclassical origins of density-functional theory (DFT) [2,3], we put forth a new idea inspired by an old method to calculate ground-state energies of many-electron systems. We start by focusing attention on the various ways in which different methods account for Pauli's principle, because the central result of our work is the observation that accurate ground-state energies can be obtained within a semiclassical framework by invoking the antisymmetry of the wave function at a late stage of the calculation, rather than from the start as present-day methods do.

In the Hartree-Fock approximation, for example, the antisymmetry requirement of the wave function enters from the very start when one chooses a single Slater determinant as ansatz for the ground-state wave function. The Hartree-Fock solution is then the determinant that minimizes the expectation value of the Hamiltonian. The antisymmetry of the wave function is also guaranteed from the start in all methods that build upon Hartree-Fock by including correlation effects either perturbatively (Moller-Plesset perturbation theory) or variationally (configuration interaction). Density-functional theory [4] deals with Pauli's principle in a more subtle way. After all, it can be formulated without ever mentioning the N-electron wave function, so its antisymmetry is encoded into the functional dependence of the energy on the ground-state density. In the Kohn-Sham scheme [5], however, the auxiliary system of noninteracting electrons is forced to satisfy Pauli's principle, reducing the work that the exchange and correlation functionals must do in order to account for the energetic consequences of antisymmetry. How orbital-free DFT [6] deals with antisymmetry can be better seen in phase space, as shown below for its precursor, the Thomas-Fermi (TF) approximation.

Thomas-Fermi theory: Two points of view.—In contemporary DFT language, the Thomas-Fermi ground-state energy E^{TF} [7,8] consists of a local-density approximation to the noninteracting kinetic-energy functional, $T_s^{\mathrm{loc}}[n]$, together with a Hartree term $U[n]$ accounting for electron-electron interactions:

$$E^{\mathrm{TF}}[n(\mathbf{r})] = T_s^{\mathrm{loc}}[n(\mathbf{r})] + U[n(\mathbf{r})] + \int d\mathbf{r}\, n(\mathbf{r}) v_{\mathrm{ext}}(\mathbf{r}). \tag{1}$$

In Eq. (1), $n(\mathbf{r})$ stands for the ground-state electron density, and $v_{\mathrm{ext}}(\mathbf{r})$ represents any external potential that might be present (e.g., the potential due to the nucleus, for an isolated atom). The kinetic-energy functional $T_s^{\mathrm{loc}}[n(\mathbf{r})] = \frac{3}{10}(3\pi^2)^{2/3}\int d\mathbf{r}\, n(\mathbf{r})^{5/3}$ is designed to yield the exact energy for a noninteracting electron gas of uniform density. The Hartree term for Coulomb-interacting electrons has the classical form $U[n(\mathbf{r})] = \frac{1}{2}\iint d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ (we use atomic units throughout).

Requiring that the energy is a minimum with respect to density variations, subject to the additional constraint that the number of particles N is fixed, $\int n(\mathbf{r}) d\mathbf{r} = N$ leads to the Thomas-Fermi equation

$$\frac{3}{10}[3\pi^2 n(\mathbf{r})]^{2/3} + v_{\mathrm{ext}}(\mathbf{r}) + v_H[n](\mathbf{r}) - \mu = 0, \tag{2}$$

where $v_H = \delta U[n]/\delta n$ is the Hartree potential, and μ is the chemical potential that guarantees satisfaction of the number constraint. The self-consistent solution of Eq. (2) produces a density that approximates the true density roughly, i.e., missing atomic shell structure, and this density in turn yields an approximate ground-state energy via Eq. (1).

But there is an alternative and equivalent way of finding E^{TF} [9]. We look at it in phase space, where important features of the Thomas-Fermi method are unveiled. Define the *classical* Hartree density of states $\rho_{\mathrm{cl}}(\varepsilon)$ as

$$\rho_{\mathrm{cl}}(\varepsilon) = \frac{1}{(2\pi)^3} \int d\mathbf{p} d\mathbf{r} \delta(\varepsilon - h_{\mathrm{cl}}(\mathbf{p}, \mathbf{r})), \tag{3}$$

where the integrals are done over all of phase space and the dynamics is governed by the classical single-particle Hamiltonian $h_{\mathrm{cl}}(\mathbf{p}, \mathbf{r}) = p^2/2 + v_{\mathrm{ext}}(\mathbf{r}) + v_H(\mathbf{r})$. Then the self-consistent solution of

$$N = \int_{-\infty}^{\varepsilon_F} \rho_{\mathrm{cl}}(\varepsilon) d\varepsilon \quad \text{and} \quad E^{\mathrm{TF}} = \int_{-\infty}^{\varepsilon_F} \varepsilon \rho_{\mathrm{cl}}(\varepsilon) d\varepsilon \tag{4}$$

leads to the same energy E^{TF} as before, Eq. (1). The Fermi energy ε_F coincides with the chemical potential $\mu = dE^{\mathrm{TF}}/dN$ of Eq. (2). How Pauli's principle is satisfied is now transparent: keep adding particles occupying each a volume h^3 of phase space [$(2\pi)^3$ in atomic units], until the available phase space has filled up. $\rho_{\mathrm{cl}}(\varepsilon)$ is the first (Weyl) term in the semiclassical Gutzwiller expansion [10] of the Kohn-Sham density of states (see, e.g., Refs. [11,12]). The smooth part of the Kohn-Sham staircase function $S_s(\varepsilon) = \sum_n \theta(\varepsilon - \varepsilon_n)$, where the ε_n are exact Kohn-Sham eigenvalues and θ is the Heaviside step function, is typically well approximated by its classical counterpart

$$S_{\mathrm{cl}}(\varepsilon) \equiv \int_{-\infty}^{\varepsilon} d\varepsilon' \rho_{\mathrm{cl}}(\varepsilon'), \tag{5}$$

as illustrated schematically in the left-hand panel of Fig. 1. While $S_{\mathrm{cl}}(\varepsilon)$ is never a poor approximation, the approximation is better for systems that behave more classically. Systems with more localized particles, such as strongly correlated systems, are one example.

It is apparent that there are two main aspects to the Thomas-Fermi approximation. First, interactions are treated in a mean-field manner. Second, it is a semiclassical approximation in the sense we have just described. Both of these approximations together lead to efficient calculations even for relatively large systems.

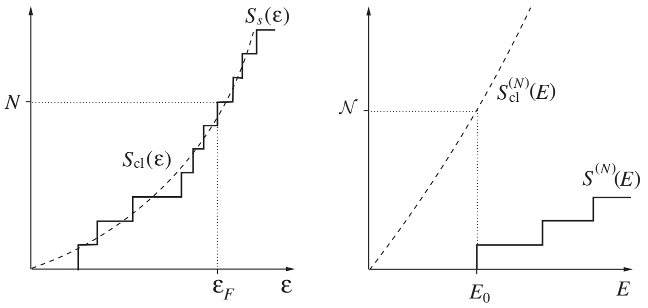

FIG. 1. Schematic diagram, assuming a spectrum with no exact degeneracies. Left-hand panel: The classical function $S_{\mathrm{cl}}(\varepsilon)$, Eq. (5), is a smooth approximation to the Kohn-Sham staircase function $S_s(\varepsilon)$. Right-hand panel: The N-electron classical function $S_{\mathrm{cl}}^{(N)}(E)$ does *not* go through the quantum N-electron staircase $S^{(N)}(E)$, because the latter consists of antisymmetric states only. $S_{\mathrm{cl}}^{(N)}(E)$ is a smooth version of the quantum-mechanical problem when symmetry is disregarded (a much steeper staircase), and can be used to approximate the true ground-state energy E_0 via Eq. (8), if the number of states $\mathcal{N}$ below the first totally antisymmetric state is known.

These two approximations are, however, separate, and therefore it should be possible to use only one. One could imagine an approximation that treats the interactions explicitly but is still semiclassical in the same sense, or one that is mean-field but not semiclassical. Any modification of this type should lead to more intensive calculations, but of course the anticipated payoff is greater insight into the system of interest. Ullmo *et al.* [13] proceed along these lines by including correction terms that take into account quantum effects that are neglected by the semiclassical form of Thomas-Fermi theory; we explore the alternate route of including interactions explicitly in a Thomas-Fermi–based framework.

Employing the notation $\mathbf{R} \equiv (\mathbf{r}_1, \ldots, \mathbf{r}_N)$, and $\mathbf{P} \equiv (\mathbf{p}_1, \ldots, \mathbf{p}_N)$, the classical N-electron density of states $\rho_{\mathrm{cl}}^{(N)}(E)$ corresponding to the classical N-electron Hamiltonian $H_{\mathrm{cl}}(\mathbf{P}, \mathbf{R})$ is

$$\rho_{\mathrm{cl}}^{(N)}(E) = \frac{1}{(2\pi)^{3N}} \int d\mathbf{P} d\mathbf{R}\, \delta(E - H_{\mathrm{cl}}(\mathbf{P}, \mathbf{R})), \tag{6}$$

and the N-electron analog of the smooth staircase function of Eq. (5) is now

$$S_{\mathrm{cl}}^{(N)}(E) \equiv \int_{-\infty}^{E} dE' \rho_{\mathrm{cl}}^{(N)}(E'). \tag{7}$$

But this function of energy does *not* go through the exact (quantum) N-electron staircase $S^{(N)}(E) = \sum_n \theta(E - E_n)$, where the E_n are the energy eigenvalues of the N-electron interacting system (see right-hand panel of Fig. 1). $S_{\mathrm{cl}}^{(N)}(E)$ typically grows much faster (factorially) than the quantum staircase because the latter consists of antisymmetric states only, and nowhere in Eqs. (6) and (7) has antisymmetry been invoked. Classical particles are distinguishable, so $S_{\mathrm{cl}}^{N}(E)$ approximates the much steeper staircase comprised of states of all symmetries (not depicted in Fig. 1). We must introduce the symmetry by counting along this steeper staircase up to the level with the correct symmetry. This is analogous to introducing the Pauli exclusion principle in standard Thomas-Fermi theory by integrating up to the Fermi energy. It is, however, a different perspective than is usually taken when finding the ground state of a fermionic system. Instead of projecting the Hamiltonian onto the correct symmetry character of the permutation group, we include all symmetries of the permutation group and convert the problem into one of state counting, that is, counting the number of states (of any symmetry) that have an energy lower than that of the first totally antisymmetric one. We call this number $\mathcal{N}$.

Knowledge of $\mathcal{N}$ yields a definite prediction for the ground-state energy as the upper limit of an energy integral:

$$\int_{-\infty}^{E^{\mathrm{CTF}}} \rho_{\mathrm{cl}}^{(N)}(E) dE = \mathcal{N}, \tag{8}$$

and we dub E^{CTF} the correlated Thomas-Fermi (CTF) approximation to E_0.

By projecting $\rho_{\mathrm{cl}}^{(N)}$ into the antisymmetric subspace, Sommerman and Weidenmueller (SW) [14] have obtained smoothed-out staircase functions that go correctly through the N-particle steps in some simple model systems, one of which we use later. But we are interested in accurate ground-state energies, and SW only yields a qualitatively good description of the antisymmetric staircase. We now try CTF in three model systems where the exact $\mathcal{N}$ can be found and then employed to obtain E^{CTF} via Eq. (8). This may seem circular, but it serves as a proof of concept that CTF can yield accurate ground-state energies when $\mathcal{N}$ is known accurately. It will also allow us to draw conclusions regarding the regimes where CTF works best.

Case 1.—First, consider two spinless electrons in a one-dimensional harmonic trap of unit frequency, interacting via a harmonic potential of frequency Ω, which we vary from 0 to 2. Figure 2 shows the energy as a function of interaction strength. The exact energy is known analytically [15]. The exact $\mathcal{N}$ is easily found to be $\mathcal{N} = \lfloor\sqrt{1 + 2\Omega^2}\rfloor + 1$, where $\lfloor\,\rfloor$ floor function, which leads to steps in the energy $E(\Omega)$. Leaving out the floor function provides the most natural way of smoothing out the CTF curve, and it is this smoothed-out curve that is depicted as the solid line in Fig. 2. We observe that the CTF results run very close to the exact curve along the whole range of interaction strengths, improving dramatically upon both TF and SW.

We have also looked at the analogous system with N up to 15 particles for $\Omega = 1$. The accuracy of CTF increases with the number of particles. The error decreases from 0.05% for $N = 3$ to 5×10^{-4}% for $N = 15$.

Case 2.—Figure 3 shows a similar trend for three spinless electrons interacting via a quartic attraction [the interaction term between two electrons is of the form $k(x_i - x_j)^4$]. Here we did an exact numerical diagonalization in order to find $\mathcal{N}$. Again, we see that CTF runs very close to the exact curve for the whole range of values of k considered.

Case 3.—Does the excellent performance of CTF reported so far have something to do with the integrability of the underlying classical dynamics (case 1) or its near-integrability (case 2)? We have also calculated the CTF energies for a simple *nonintegrable* system, 2 electrons interacting via a soft-Coulomb potential $1/\sqrt{1 + (x_1 - x_2)^2}$ in a 1D box of length L. In spite of the apparent simplicity of this model, the importance of ergodicity can be assessed as the length of the box is increased. Indeed, as concluded in Ref. [16], this system displays hard chaos in the large-box limit, closely related to the fact that, due to the low electron density in that limit, the system becomes strongly correlated with the electrons localizing in opposite extremes of the box. Table I shows the numbers obtained when the same value of $\mathcal{N} = 2$ is used for different box lengths. The performance of CTF improves as L increases, due to the increased localization leading to greater classical character. This suggests that CTF might be particularly useful in the strongly correlated regime.

Adding spin does not require fundamental modifications of the procedure. Because only the combined spatial and spin function must be antisymmetric, the constraint on the spatial wave function to be totally antisymmetric is dropped. Since the spin function consists of combinations of only up and down spins, not all symmetries are allowed. The goal then is to find the symmetry of the ground state and use it when finding $\mathcal{N}$. The pouring theorem of Lieb and Mattis [17] is useful in determining possible permutation group character of the ground state. Once this is

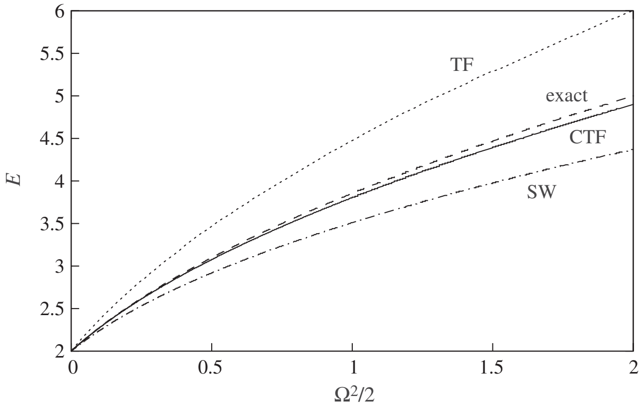

FIG. 2. Ground-state energy for two spinless electrons interacting in one dimension via the potential $\frac{1}{2}\Omega^2(x_1 - x_2)^2$, calculated exactly (dashed line) and by different approximations: standard Thomas-Fermi (dotted line), employing the antisymmetric staircase of SW [14] (dot-dashed line), and our CTF (solid line).

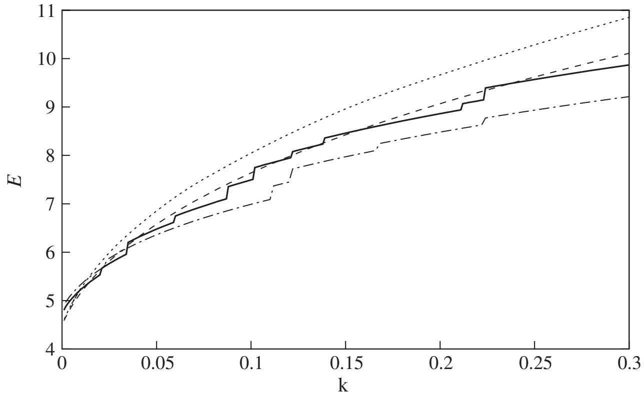

FIG. 3. Ground-state energy for three spinless electrons interacting in one dimension via the potential $k(x_i - x_j)^4$, calculated exactly (dashed line) and by different approximations: standard Thomas-Fermi (dotted line), our CTF method (solid line), and CTF when the number of states $\mathcal{N}$ below the first totally antisymmetric state is calculated from perturbation theory (dot-dashed line).

TABLE I. Exact, TF, and CTF ($\mathcal{N} = 2$) ground-state energies for two electrons interacting via a soft-Coulomb potential $[(x_1 - x_2)^2 + 1]^{-1/2}$ and confined in a box of length L atomic units.

L	TF	CTF ($\mathcal{N} = 2$)	Exact
1	1.37×10^1	1.35×10^1	2.56×10^1
10	2.75×10^0	4.38×10^{-1}	5.12×10^{-1}
100	2.31×10^0	2.05×10^{-2}	2.20×10^{-2}
1000	1.99×10^0	1.40×10^{-3}	1.45×10^{-3}

determined, the method follows the analogous procedure already described.

Finally, we turn to the problem of finding $\mathcal{N}$. Any actual practical application of CTF will require a solution to this problem. The naive idea of employing the single-particle density of states to estimate $\mathcal{N}$ as

$$\mathcal{N} \sim \mathcal{N}^{\mathrm{TF}} = \int_{-\infty}^{E^{\mathrm{TF}}} \rho_{\mathrm{cl}}(\varepsilon) d\varepsilon, \tag{9}$$

in analogy to Eq. (8), is not adequate. To see this, consider N electrons in a harmonic well of frequency ω interacting harmonically, as before, with strength Ω. We find $E^{\mathrm{TF}} = N^2\sqrt{\omega^2 + \Omega^2 N}/2$, and Eq. (9) leads to $\mathcal{N}^{\mathrm{TF}} = E^{\mathrm{TF}}/\sqrt{\omega^2 + \Omega^2 N} = N^2/2$, a result independent of the interaction strength Ω. But the actual value of $\mathcal{N}$ depends on Ω. We observe the same behavior for the three quartically interacting electrons, where an almost Ω-independent value of $\mathcal{N}$ was found numerically via Eq. (9). The $\Omega \to 0$ limit of $\mathcal{N}$, however, is correctly given by Eq. (9). For cases 1 and 2, this limit is equal to 2 and 18, respectively.

A straightforward way of approximating $\mathcal{N}$ is using the number of states before the first totally antisymmetric state as given by perturbation theory. The missing of avoided crossings is not too important because the *order* of states before the first antisymmetric one is irrelevant. It is only the *number* of states in this window that matters. Figure 3 shows the results obtained by using $\mathcal{N}$ from perturbation theory.

The perturbation method of finding $\mathcal{N}$ is most accurate in the weakly correlated regime. CTF is expected to have an advantage for strongly correlated systems, and using perturbation theory to evaluate $\mathcal{N}$ would reduce this advantage. It makes sense therefore to consider using an asymptotic expansion from the strictly correlated limit [18]. In this limit the electronic wave functions become delta functions centered at the points that would lead to a minimization of the classical electrostatic potential energy. The energy levels in this limit can therefore be approximated by expanding the potential energy term around these points up to second order. This leads to a multiple harmonic oscillator problem which can be solved, and which for strongly correlated systems should give a fair approximation for $\mathcal{N}$. This is where our research efforts will go now.

As explained in Ref. [12], the correlation energy for an N-electron system is not readily accessible from semiclassical Wigner-Kirkwood expansions [19] or related techniques [20]. These methods are normally employed to obtain approximate density functionals for the Kohn-Sham density matrix, from which all but the "correlation" pieces of the energy can be easily constructed. It is the N-body Green function, rather than the Kohn-Sham one, that must be used as input to obtain approximate correlation energies. Our CTF results suggest that this route to correlation energies is worth exploring.

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