

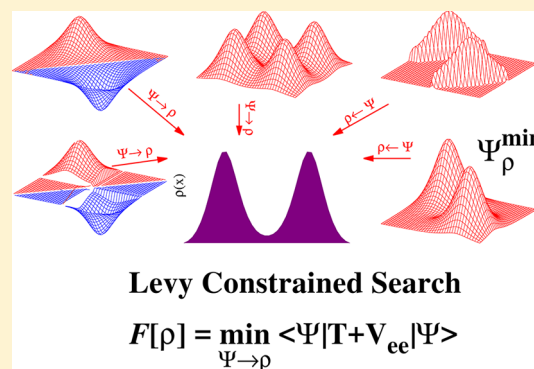
Exact Density Functional Obtained via the Levy Constrained Search

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ABSTRACT: A stochastic minimization method for a real-space wave function, $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, constrained to a chosen density, $\rho(\mathbf{r})$, is developed. It enables the explicit calculation of the Levy constrained search, $F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$, which gives the exact functional of density functional theory. This general method is illustrated in the evaluation of $F[\rho]$ for densities in one dimension with a soft-Coulomb interaction. Additionally, procedures are given to determine the first and second functional derivatives, $\delta F / \delta \rho(\mathbf{r})$ and $\delta^2 F / [\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')]$. For a chosen external potential, $v(\mathbf{r})$, the functional and its derivatives are used in minimizations over densities to give the exact energy, E_v , without needing to solve the Schrödinger equation.



The electron density, $\rho(\mathbf{r})$, is the central object of density functional theory (DFT). The foundational theorems^{1,2} prove the existence of one universal functional in the space of densities, $F[\rho]$, that contains the necessary information to give the exact many-body ground-state energy of all possible systems. In virtually all calculations in the literature, the map is approximated within the context of a Kohn–Sham (KS) noninteracting reference³ with approximate functionals such as PBE and B3LYP.^{4,5} However, the exact map, $F[\rho]$, utilizes the exact many-body wave function, $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$, where $\rho(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N$, and does not involve KS. The Levy constrained search² is defined by considering only many-body wave functions that integrate to the same one-electron density, $\Psi \rightarrow \rho$, to define the exact density functional

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \quad (1)$$

For each given density, $\rho(\mathbf{r})$, there is a minimizing wave function, Ψ_{ρ}^{\min} , and one value of the functional, $F[\rho] = \langle \Psi_{\rho}^{\min} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho}^{\min} \rangle$. The whole formalism is constructed to be completely independent of any potential, $v(\mathbf{r})$, or the more complicated question of whether the $\rho(\mathbf{r})$ is the ground state of a potential (v -representability).

However, this one universal functional can be used in a minimization solely over the space of all possible densities to give the exact ground-state many-body energy of the Schrödinger equation for every external potential

$$E_v[\rho] = \min_{\rho} \left\{ F[\rho] + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right\} \quad (2)$$

These are the foundational equations of DFT; however, they have not been directly numerically realized. There has been other work on the exact functional via a Lieb maximization⁶ which gives the ensemble constrained search result of Valone.⁷

The Lieb maximizations carry out a search over potentials on which to carry out a many-body method such as full configuration interaction (FCI)^{8–13} and in time-dependent DFT.^{14,15} However, the Lieb maximization would fail to converge if the density is non- v -representable, and the search over potentials becomes much harder as the density becomes more strongly correlated.^{11,16} Also, there have been direct Monte Carlo proposals to tackle the constrained search.^{17,18}

In this Letter, we develop a method to explicitly carry out the Levy constrained search over many-body wave functions that integrate to the same density, $\Psi \rightarrow \rho$ as in eq 1 and, furthermore, to carry out the minimization over densities in eq 2, as an alternative to solving the Schrödinger equation. The importance of the exact functional is demonstrated for strongly correlated systems.

To carry out the constrained search to a target density, denoted as ρ_{target} , we develop a stochastic procedure that contains four key steps:

- (1) Construct an initial wave function, Ψ_{initial} , that integrates to ρ_{target} .
- (2) Take a trial step in wave function space that maintains integration to ρ_{target} .
- (3) Evaluate the many-body energy of this trial wave function.
- (4) Accept or reject step and return to step 2 until convergence.

The fundamental aspect of this method is to define appropriate movements in wave function space that keep the integration to the same density in step 2. Consider an N -

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electron Fermionic wave function that can be separated into a spatial part, $\Psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N)$, multiplied by a fixed spin part, $\sigma(s_1, s_2 \dots s_N)$. A change in $\Psi(\mathbf{R})$ at one point in Hilbert space $\mathbf{R} = \mathbf{R}_1, \mathbf{R}_2 \dots \mathbf{R}_N$ changes the density at N separate points $\rho(\mathbf{R}_1), \rho(\mathbf{R}_2) \dots \rho(\mathbf{R}_N)$. A second chosen point is needed, $\mathbf{R}' = \mathbf{R}'_1, \mathbf{R}'_2 \dots \mathbf{R}'_N$, where $\mathbf{R}'_i \neq \mathbf{R}_i$ or \mathbf{R}_2 or $\mathbf{R}_3 \dots$ or $\mathbf{R}_N \forall i$. Next, define a replacement operator \hat{P}_i which replaces \mathbf{R}_i by \mathbf{R}'_i , and take all possible replacements of the original wave function, $\Psi_{l_1 l_2 \dots l_N} = \Psi(\Pi_{i=1}^N \hat{P}_i \mathbf{R})$, with $l_i = 0$ or 1. Using this collections of wave functions, it is possible to construct a move that does not modify the density, $\Psi_{l_1 l_2 \dots l_N}^2 \rightarrow \Psi_{l_1 l_2 \dots l_N}^2 + (-1)^{\sum_i l_i} \Delta$ for all binary numbers $l_1 l_2 \dots l_N$ from 00...0 up to 11...1. The combined move changes 2^N points of the original wave function (and all its symmetric or antisymmetric mirrored parts) while maintaining the integration to ρ_{target} . This overall procedure illustrates the principle of many different real-space wave functions, with different values of $\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$, that all yield identical densities, which is the key to performing the Levy constrained search.

For other wave functions which are not separable, it is possible to define similar moves by enforcing antisymmetry on electrons of the same spin. For example, for a doublet three-electron wave function, $\Psi^{3e}(x_1, x_2, x_3)$, antisymmetry is enforced between x_1 and x_2 and not with x_3 . In this case, the total density is given by $\rho(x) = 2 \int \Psi^2(x_1, x_2, x_3) dx_2 dx_3 + \int \Psi^2(x_1, x_2, x_3) dx_1 dx_2$, and a sample move would be $\Psi_{000}^2 + \Delta$, $\Psi_{100}^2 \rightarrow \Psi_{100}^2 - \Delta$ for $\Psi_1 = \{\Psi_{100}, \Psi_{010}, \Psi_{001}\}$, $\Psi_2^2 \rightarrow \Psi_2^2 + \Delta$ for $\Psi_2 = \{\Psi_{110}, \Psi_{101}, \Psi_{011}\}$ and $\Psi_{111}^2 \rightarrow \Psi_{111}^2 - \Delta$, as illustrated in Figure 1b with another possible move in Figure 1c.

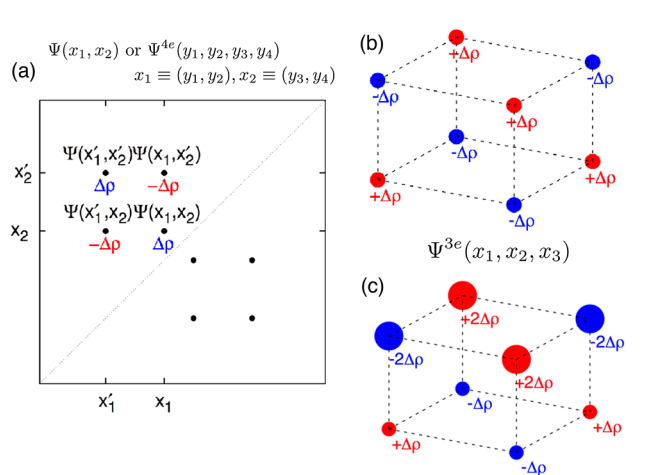


Figure 1. Example moves that maintain integration of a wave function to a target density: (a) two-electron singlet (bottom right moved symmetrically), two-electron triplet (bottom right moved antisymmetrically), and four-electron singlet involving double excitations; (b and c) three-electron doublet.

To demonstrate this overall method for an explicit Levy constrained search, we examine densities in one dimension, $\rho(x)$. The one-dimensional universe is described, as in previous work,^{19,20} using a real space grid with a softened Coulomb interaction, $\hat{V}_{ee}(x_1, x_2) = 1/\sqrt{(x_1 - x_2)^2 + 1}$ and $\hat{T} = -\frac{1}{2} \frac{d^2}{dx^2}$. This main body of work focuses on two-electron systems, where the overall wave function is antisymmetric and separable, $\Psi(x_1, s_1, x_2, s_2) = \Psi(x_1, x_2) \sigma(s_1, s_2)$, with spin parts

being the singlet or triplet, $\sigma(s_1, s_2) = \frac{1}{\sqrt{2}}(\alpha(s_1)\beta(s_2) \mp \alpha(s_2)\beta(s_1))$.

Regarding the construction of Ψ_{initial} in step 1, for the singlet state $\Psi_{\text{initial}}(x_1, x_2) = \Psi_{\text{KS}} = \sqrt{\rho(x_1)\rho(x_2)}/2$, and for the triplet state a Gilbert construction²¹ with a direct division of space gives two orbitals such that ${}^3\Psi_{\text{initial}}(x_1, x_2) = [\phi_1(x_1) - \phi_2(x_2) - \phi_2(x_1)\phi_1(x_2)]/\sqrt{2}$. In this case, to define the appropriate movements of the wave function in step 2, we consider $\mathbf{R} = x_1, x_2$ and move the wave function by a small amount, $\epsilon_{x_1 x_2} \Psi^{\text{trial}}(x_1, x_2) = \Psi(x_1, x_2) + \epsilon_{x_1 x_2}$, with a change in the density, $\Delta\rho_{x_1 x_2}$ at two points, x_1 and x_2 of

$$\Delta\rho_{x_1 x_2} = \epsilon_{x_1 x_2}^2 + 2\epsilon_{x_1 x_2} \Psi(x_1, x_2) \quad (3)$$

Thus, we randomly take another point $\mathbf{R}' = x'_1, x'_2 \neq x_1$ or x_2 , and consider moves of the wave function at $\Psi^{\text{trial}}(x_1, x'_2) = \Psi(x_1, x_2) + \epsilon_{x_1 x'_2}$, $\Psi^{\text{trial}}(x'_1, x_2) = \Psi(x_1, x_2) + \epsilon_{x'_1 x_2}$, and $\Psi^{\text{trial}}(x'_1, x'_2) = \Psi(x_1, x_2) + \epsilon_{x'_1 x'_2}$. The amount by which the wave function has to move at each of these points is found by solving the quadratic equations

$$\epsilon_{x_i x_j}^2 + 2\Psi(x_i, x_j)\epsilon_{x_i x_j} - \Delta\rho_{x_i x_j} = 0 \quad (4)$$

with $\Delta\rho_{x_i x'_i} = \Delta\rho_{x'_i x_i} = -\Delta\rho$ and $\Delta\rho_{x'_i x'_i} = \Delta\rho$. For the case of $x_1 = x_2 = x$, an alternative move is used with $\Delta\rho_{x x'} = \Delta\rho_{x' x} = \Delta\rho_{x x''} = \Delta\rho_{x'' x} = -\Delta\rho/2$ and $\Delta\rho_{x' x''} = \Delta\rho_{x'' x'} = \Delta\rho/2$. The first of these movements is pictured in Figure 1a. If the solution of any of the quadratic equations (eq 4) has no real roots, the whole move is rejected. Otherwise, the trial energy, $E^{\text{trial}} = \langle \Psi^{\text{trial}} | \hat{T} + \hat{V}_{ee} | \Psi^{\text{trial}} \rangle$, is evaluated such that if it is lower than the current energy, the step is accepted and otherwise it is rejected (steps 3 and 4). This procedure is carried out many times to optimize the wave function. The best scheme we have found initially uses a very small random move in the wave function, $-10^{-10} \leq \epsilon \leq 10^{-10}$, $|\epsilon| > 10^{-14}$, and if a step is successful, a simple line-search is carried out by multiplying the size of the step by 10, but with the same x_1, x_2, x'_1 , and x'_2 (or $x, x',$ and x''), and this is repeated until the move is rejected.

This method allows us to carry out the constrained search efficiently and to calculate the exact functional for any density. For example, Figure 2 shows a variety of wave functions that yield the same target one-dimensional density. The minimizing singlet and triplet wave functions (Ψ_{ρ}^{min} and ${}^3\Psi_{\rho}^{\text{min}}$) are found by carrying out the constrained search as outlined above. Convergence is found in 5000 stochastic cycles over the wave function, each cycle consisting of an attempted move at each point of the wave function.

We also carry out calculations for some doublet three-electron and singlet four-electron systems, for which the wave functions are no longer separable into a space and spin part but are simply treated by maintaining antisymmetry within the same spin electrons as described above. A similar procedure as described for the two-electron case is used, though an increased number of stochastic steps is needed because of the greater number of variables in the wave function as the dimensionality of the system increases. However, we are still routinely able to achieve convergence to μ Hartree accuracy in 50 000 stochastic cycles. Similar convergence to the two-electron case as shown in Figure 2 is obtained with energy

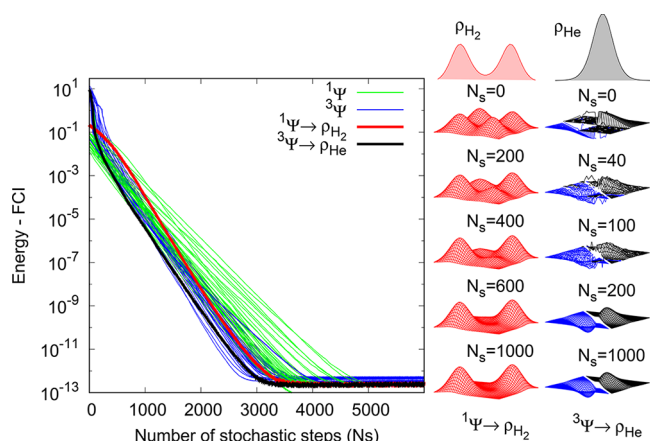


Figure 2. Convergence of the energy of the Levy constrained search to the FCI energy during the stochastic optimization of the wave function for 100 different randomly chosen molecular densities. Highlighted is the convergence for H₂ at $R = 5$ with singlet wave functions (red) and He with triplet wave functions (black).

differences from the FCI energy of $2 \times 10^{-7} E_h$ and $9 \times 10^{-6} E_h$, for 3 and 4 electrons, respectively.

Calculation of the Levy constrained search for one density gives one point of $F[\rho]$, which in its entirety is a unique high-dimensional surface in the \mathcal{R} -dimensional space of densities. For example, in a 100 grid point representation of x , the space of two-electron densities, $\rho(x)$, would be 99 dimensional, and $F[\rho(x)]$ can be considered as a 99 dimensional function. Such a high-dimensional object cannot be visualized, but relevant cuts in restricted spaces can be considered. For example, in Figure 3, the landscape of the exact functional is shown for a

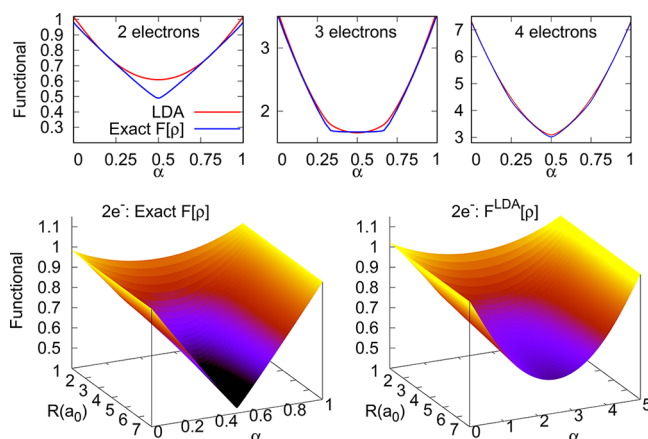


Figure 3. Cut of the landscape of the exact density functional for $\rho(\alpha, R) = N/2[\alpha\rho_{\text{He}}(0) + (1 - \alpha)\rho_{\text{He}}(R)]$, compared with the LDA functional. This highlights how the derivative discontinuity²² of $F[\rho]$ develops with increasing separation between two atoms. The top three figures are at $R = 5$ for different numbers of electrons, $N = 2, 3$, and 4.

two-dimensional slice of densities that are a convex linear combinations of two He densities at a distance R , $\rho(\alpha, R) = N/2[\alpha\rho_{\text{He}}(0) + (1 - \alpha)\rho_{\text{He}}(R)]$ ($0 \leq \alpha \leq 1$) (for $N = 2, 3$, and 4), where $\rho_{\text{He}}(R)$ is a 1d-Helium atom density centered at R , and α corresponds to the electron-transfer coordinate between the two sites. For two electrons, $\alpha = 0$ and $\alpha = 1$ are Helium atoms centered at different points and $\alpha = 0.5$ corresponds to an H₂-like density, whereas other values of α give fractional

numbers of electrons on the two centers. As the distance is increased, the density becomes more strongly correlated, showing a very large difference between the LDA and exact values of the functional ($\Delta F = 0.139 E_h = 90 \text{ kcal/mol}$, for $R = 7$ and $\alpha = 0.5$), which is exactly the static correlation error of systems like stretched H₂. However, much more important is the global behavior on varying α . At shorter distances, LDA behaves similarly to the exact functional, but as the distance is increased, it exhibits a failure to describe the v-shape of the exact functional with a qualitatively incorrect second derivative related to its missing derivative discontinuity.²² It is this failure in the $F^{\text{LDA}}[\rho]$ surface that leads to the incorrect description of charge transfer in strongly correlated systems with DFT approximations.²³ It is now clear what key feature of the functional needs to be reproduced to correctly describe strongly correlated charge transfer.

The inherent complexity of the exact functional, $F[\rho]$, has often lead to conceptualizing it as an algorithm to give one number for a chosen density. In addition to this view, it is important to understand the functional as a surface in the space of densities, and one of the defining concepts of a surface is differentiability. Previously, it has been argued that the exact Lieb functional (and the same would apply to the Levy functional) is nongateaux differentiable everywhere.²⁴ This argument, however, does not apply to the density on a finite grid, and consequently, we show how to calculate the exact functional derivatives, $\frac{\delta F[\rho]}{\delta \rho(x)}$ and $\frac{\delta^2 F[\rho]}{\delta \rho(x) \delta \rho(x')}$.

The first functional derivative can be determined from the converged wave function, as it has been minimized to variations at fixed density, $\left(\frac{\delta F}{\delta \Psi}\right)_{\rho} = \left(\frac{\delta(\Psi^{\text{min}} \hat{T} + \hat{V}_{ee} \Psi^{\text{min}})}{\delta \Psi}\right)_{\rho} = 0$.

Thus, differentiation with respect to $\Psi(x_1, x_2)$ gives the Schrödinger-like equation:

$$(\hat{T} + \hat{V}_{ee})\Psi(x_1, x_2) = \left(\frac{\delta F}{\delta \rho(x_1)} + \frac{\delta F}{\delta \rho(x_2)}\right)\Psi(x_1, x_2) \quad (5)$$

Multiplying by $\Psi(x_1, x_2)$ and integrating (summing) over x_2 gives a matrix equation

$$h_{x_1} = \sum_{x_2} M_{x_1 x_2} d_{x_2} \quad (6)$$

where $d_{x_2} = \frac{\delta F}{\delta \rho(x_2)}$, $M_{x_1 x_2} = \Psi^2(x_1, x_2) + \frac{1}{2}\rho(x_1)\delta_{x_1 x_2}$, and $h_{x_1} = \int \Psi(x_1, x_2)(\hat{T} + \hat{V}_{ee})\Psi(x_1, x_2) dx_2$. Solution of these simultaneous equations at $\Psi(x_1, x_2) = \Psi_{\rho}^{\text{min}}(x_1, x_2)$ by inversion of the \mathbf{M} matrix gives the functional derivative.

Another way to calculate the first derivative is to make a set of changes $\{\Delta_i\}$ to the density, defined by

$$\Delta_i(x) = \begin{cases} \Delta_i(x_i) = 10^{-6} \\ \Delta_i(x_j) = \frac{2 - \rho(x_i) - 10^{-6}}{2 - \rho(x_i)} \rho(x_j) \quad \forall j \neq i \end{cases} \quad (7)$$

This is a small movement in the density at x_i , that is compensated by moving all other points of the density the opposite way, such that the overall normalization does not change, $\int \Delta_i(x) dx = 0$. The vectors of the finite difference approximation are formed

$$\lim_{\epsilon \rightarrow 0} \left\{ \frac{F[\rho + \epsilon \Delta_i] - F[\rho]}{\epsilon} \right\} = F_i = \int \frac{\delta F[\rho]}{\delta \rho(x)} \Delta_i(x) dx \quad (8)$$

giving the set of equations

$$F_k = \sum_x v_x \Delta_{kx} \quad (9)$$

that is solved by construction of the pseudoinverse, Δ_{kx}^{-1} , and applying it on the F_k vector. The same machinery enables the calculation of the second derivatives

$$\lim_{\epsilon \rightarrow 0} \left\{ \frac{\frac{\delta F[\rho + \epsilon \Delta_i]}{\delta \rho(x)} - \frac{\delta F[\rho]}{\delta \rho(x)}}{\epsilon} \right\} = \int \frac{\delta^2 F[\rho]}{\delta \rho(x) \delta \rho(y)} \Delta_i(y) dy \quad (10)$$

By constructing the potential $v_i(x)$ corresponding to the density $\rho + \Delta_p$ the second-derivative Hessian matrix is built

$$\frac{\delta^2 F[\rho]}{\delta \rho(x) \delta \rho(y)} = \Delta_{ky}^{-1} [v_k(x) - v(x)] \quad (11)$$

The Hessian matrix can be diagonalized, and if a negative eigenvalue is found, the functional would be concave and it would correspond to a non- v -representable density (see for example the Supplemental Material of ref 25).

The minimization of the energy in eq 2 can now be carried out and treated as a general optimization problem using the analytic first and second derivatives, $g_y = -\frac{\delta F[\rho]}{\delta \rho(y)}$ and $H_{xy} = \frac{\delta^2 F[\rho]}{\delta \rho(x) \delta \rho(y)}$. Therefore, for a given potential, $v_y = v(y)$, to best change $\rho(x)$ to minimize the energy, a Newton step, $H^{-1}g$, is taken

$$\Delta \rho(x) = m \left(\frac{\delta^2 F}{\delta \rho(x) \delta \rho(y)} \right)^{-1} \left(-\frac{\delta F}{\delta \rho(y)} - v(y) \right) + C \quad (12)$$

where the constant, C , enforces that the density is normalized, $\int \Delta \rho(x) dx = 0$. Usually $m = 1$, though if the step is not valid, i.e., $\rho(x) + \Delta \rho(x) \not\geq 0 \forall x$, a scaled down step with $m = 0.1$ is taken. This is needed only in the first few steps of the optimization. None of the optimizations we have performed have needed more than 35 steps, and all of them have converged no matter what the starting density is, as illustrated in Figure 4.

In conclusion, we have explicitly carried out the Levy constrained search using a stochastic optimization to give the exact functional of DFT, $F[\rho]$. Millions of many-body wave functions are searched, all integrating to the same $\rho(\mathbf{r})$, and the minimizing wave function that yields that $\rho(\mathbf{r})$ and gives the lowest possible value of $\langle \Psi_\rho | \hat{T} + \hat{V}_{ee} | \Psi_\rho \rangle$ is found. Moreover, from this minimizing wave function, the first and second functional derivatives are constructed and used in a direct optimization of the total energy in density space for any external potential. Thus, the exact many-body energy is obtained without solving the Schrödinger equation, and rapid convergence is seen from any starting density, including strongly correlated systems. It is important to view the exact functional as a calculable surface in density space, as illustrated in Figure 3, highlighting many avenues for future investigation, from the adiabatic connection²⁶ to the critical question of how to build more accurate approximations to $F[\rho]$.

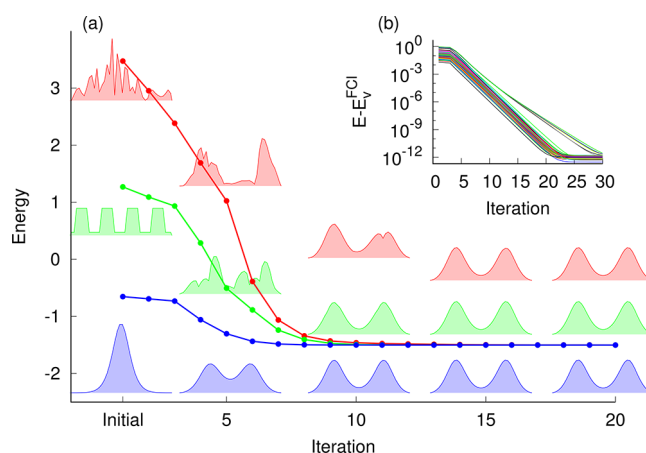


Figure 4. (a) Convergence of the energy and density for a one-dimensional H_2 potential (FCI energy = -1.500653), starting from three different initial densities: random (red), step-like (green), and He atom (blue). Inset (b) shows the convergence of the energy to the FCI value for 100 different random molecular potentials, $v(x) = -Z/\sqrt{x^2 + a} - Y/\sqrt{(x-R)^2 + a}$.

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Notes

The authors declare no competing financial interest.

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