

Supplementary Information to “Landscape of the exact energy functional”

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A. Derivation of Eq. (13)

To derive the exact functional,

$$F^{\text{Levy}} = \min_{\Psi \rightarrow \gamma} \langle \Psi | V_{ee} | \Psi \rangle \quad (\text{S1})$$

consider the minimization over real singlet wavefunctions

$$\begin{aligned} \Psi = \frac{a}{\sqrt{2}} [\mathcal{A}(\phi_1\alpha\phi_2\beta) + \mathcal{A}(\phi_2\alpha\phi_1\beta)] \\ + b\mathcal{A}(\phi_1\alpha\phi_1\beta) + c\mathcal{A}(\phi_2\alpha\phi_2\beta). \end{aligned} \quad (\text{S2})$$

in terms of the parameters a, b and c along with the normalization $a^2 + b^2 + c^2 = 1$ and the elements of the density-matrix $\gamma_{ij} = \sum_{\sigma} \langle \Psi | c_{i\sigma}^{\dagger} c_{j\sigma} | \Psi \rangle$ giving $\gamma_{11} = 2b^2 + a^2$ and $\gamma_{12} = \sqrt{2}(ba + ac)$. The two-electron energy comes only from the $\langle 11|11 \rangle$ and $\langle 22|22 \rangle$ integrals, which are U , as all other integrals are 0, so only the second determinant with itself and the third determinant with itself contribute, giving

$$F[\Psi] = U(b^2 + c^2) = U(1 - a^2) \quad (\text{S3})$$

It is also satisfied that

$$\gamma_{11} - 1 = b^2 - c^2. \quad (\text{S4})$$

Therefore, using γ_{12} gives

$$(b + c) = \frac{\gamma_{12}}{\sqrt{2}a} \quad (\text{S5})$$

and combining with Eq. (S4) leads to

$$(b - c) = \frac{(\gamma_{11} - 1) \sqrt{2}a}{\gamma_{12}} \quad (\text{S6})$$

Now, square Eqs. (S5) and (S6), to give

$$(b + c)^2 = \frac{\gamma_{12}^2}{2a^2} \quad (\text{S7})$$

and

$$(b - c)^2 = \frac{(\gamma_{11} - 1)^2 2a^2}{\gamma_{12}^2}. \quad (\text{S8})$$

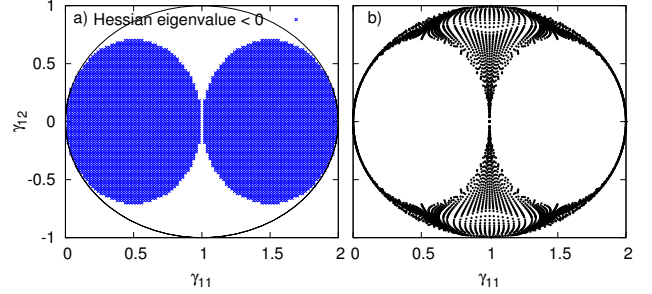


Figure S1: The plane of all possible density matrices illustrating the non- v -representability of many of the allowable γ . a) The second derivatives of the exact functional showing the points where the lowest hessian eigenvalue is < 0 from Eqs S14-S16 and b) the density matrices, γ , achieved in 6552 FCI calculations for $-10 < t < 10$ and $-10 < \Delta\epsilon < 10$.

Adding these two has the result

$$2b^2 + 2c^2 = \frac{\gamma_{12}^2}{2a^2} + \frac{(\gamma_{11} - 1)^2 2a^2}{\gamma_{12}^2}. \quad (\text{S9})$$

Using the normalization, gives

$$(2 - 2a^2) = \frac{\gamma_{12}^2}{2a^2} + \frac{(\gamma_{11} - 1)^2 2a^2}{\gamma_{12}^2} \quad (\text{S10})$$

which leads to a quadratic equation for a^2

$$\frac{[(\gamma_{11} - 1)^2 + \gamma_{12}^2]}{\gamma_{12}^2} a^4 - a^2 + \frac{\gamma_{12}^2}{4} = 0 \quad (\text{S11})$$

with solution

$$a^2 = \frac{\gamma_{12}^2 \left(1 \pm \sqrt{1 - (\gamma_{11} - 1)^2 - \gamma_{12}^2} \right)}{2[(\gamma_{11} - 1)^2 + \gamma_{12}^2]}. \quad (\text{S12})$$

Taking the plus combination gives the lowest energy

$$\begin{aligned} E &= 1 - a^2 \\ &= 1 - \frac{\gamma_{12}^2 \left(1 + \sqrt{1 - (\gamma_{11} - 1)^2 - \gamma_{12}^2} \right)}{2[(\gamma_{11} - 1)^2 + \gamma_{12}^2]} \\ &= \frac{2[(\gamma_{11} - 1)^2 + \gamma_{12}^2] - \gamma_{12}^2 \left(1 + \sqrt{1 - (\gamma_{11} - 1)^2 - \gamma_{12}^2} \right)}{2[(\gamma_{11} - 1)^2 + \gamma_{12}^2]} \\ &= \frac{2(\gamma_{11} - 1)^2 + \gamma_{12}^2 \left(1 - \sqrt{1 - (\gamma_{11} - 1)^2 - \gamma_{12}^2} \right)}{2[(\gamma_{11} - 1)^2 + \gamma_{12}^2]}. \end{aligned} \quad (\text{S13})$$

This agrees with Eq. (13) of the paper.

The derivatives of the exact functional can be evalu-

ated analytically and are used in Fig. S1.

$$\frac{\partial E}{\partial \gamma_{11}} = \frac{4(\gamma_{11} - 1) + (\gamma_{11} - 1)\gamma_{12}^2/\sqrt{1 - (\gamma_{11} - 1)^2 - \gamma_{12}^2}}{2((\gamma_{11} - 1)^2 - \gamma_{12}^2)} - \frac{(\gamma_{11} - 1) \left(2(\gamma_{11} - 1)^2 + \gamma_{12}^2 \left(1 - \sqrt{1 - (\gamma_{11} - 1)^2 - \gamma_{12}^2} \right) \right)}{[(\gamma_{11} - 1)^2 + \gamma_{12}^2]^2}$$

and

$$\frac{\partial E}{\partial \gamma_{12}} = \frac{\gamma_{12}^3/\sqrt{1 - (\gamma_{11} - 1)^2 - \gamma_{12}^2} + 2\gamma_{12} \left(1 - \sqrt{1 - (\gamma_{11} - 1)^2 - \gamma_{12}^2} \right)}{2((\gamma_{11} - 1)^2 + \gamma_{12}^2)} - \frac{2\gamma_{12}(\gamma_{11} - 1)^2 + \gamma_{12}^3\sqrt{1 - (\gamma_{11} - 1)^2 - \gamma_{12}^2}}{[(\gamma_{11} - 1)^2 + \gamma_{12}^2]^2}.$$

$$\begin{aligned} \frac{\partial^2 E}{\partial^2 \gamma_{11}^2} = & \frac{-4(\gamma_{11} - 1)^2 ((\gamma_{11} - 1)^2 + \gamma_{12}^2) \left(\frac{\gamma_{12}^2}{\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2}} + 4 \right) + 8(\gamma_{11} - 1)^2 \left(2(\gamma_{11} - 1)^2 - \gamma_{12}^2 \left(\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2} - 1 \right) \right)}{2((\gamma_{11} - 1)^2 + \gamma_{12}^2)^3} \\ & + \frac{((\gamma_{11} - 1)^2 + \gamma_{12}^2)^2 \left(4 - \frac{\gamma_{12}^2(\gamma_{12}^2 - 1)}{(-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2)^{3/2}} \right) - 2((\gamma_{11} - 1)^2 + \gamma_{12}^2) \left(2(\gamma_{11} - 1)^2 - \gamma_{12}^2 \left(\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2} - 1 \right) \right)}{2((\gamma_{11} - 1)^2 + \gamma_{12}^2)^3} \end{aligned} \quad (\text{S14})$$

$$\begin{aligned} \frac{\partial^2 E}{\partial \gamma_{11} \partial \gamma_{12}} = & \frac{(\gamma_{11} - 1)\gamma_{12} \left(-2\gamma_{11}^6 + 12\gamma_{11}^5 + 2\gamma_{11}^2 \left(10\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2} - 9\gamma_{12}^2 + 1 \right) - 4\gamma_{11} \left(2\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2} - 3\gamma_{12}^2 + 1 \right) \right)}{2(-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2)^{3/2} (\gamma_{11}^2 - 2\gamma_{11} + \gamma_{12}^2 + 1)^3} \\ & - \frac{(\gamma_{11} - 1)\gamma_{12} \left(\gamma_{12}^2 \left(-2\gamma_{12}^2 \left(2\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2} + 3 \right) + 4\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2} + \gamma_{12}^4 + 1 \right) \right)}{2(-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2)^{3/2} (\gamma_{11}^2 - 2\gamma_{11} + \gamma_{12}^2 + 1)^3} \\ & - \frac{(\gamma_{11} - 1)\gamma_{12} \left(+\gamma_{11}^4 \left(4 \left(\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2} - 6 \right) - 3\gamma_{12}^2 \right) - 4\gamma_{11}^3 \left(4\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2} - 3\gamma_{12}^2 - 4 \right) \right)}{2(-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2)^{3/2} (\gamma_{11}^2 - 2\gamma_{11} + \gamma_{12}^2 + 1)^3} \end{aligned} \quad (\text{S15})$$

$$\begin{aligned} \frac{\partial^2 E}{\partial^2 \gamma_{12}^2} = & \frac{-4\gamma_{12}^2 ((\gamma_{11} - 1)^2 + \gamma_{12}^2) \left(\frac{\gamma_{12}^2}{\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2}} - 2\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2} + 2 \right)}{2((\gamma_{11} - 1)^2 + \gamma_{12}^2)^3} \\ & + \frac{8\gamma_{12}^2 \left(2(\gamma_{11} - 1)^2 - \gamma_{12}^2 \left(\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2} - 1 \right) \right) - 2((\gamma_{11} - 1)^2 + \gamma_{12}^2) \left(2(\gamma_{11} - 1)^2 - \gamma_{12}^2 \left(\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2} - 1 \right) \right)}{2((\gamma_{11} - 1)^2 + \gamma_{12}^2)^3} \\ & + \frac{((\gamma_{11} - 1)^2 + \gamma_{12}^2)^2 \left(\frac{5\gamma_{12}^2}{\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2}} - 2\sqrt{-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2} + \frac{\gamma_{12}^4}{(-\gamma_{11}^2 + 2\gamma_{11} - \gamma_{12}^2)^{3/2}} + 2 \right)}{2((\gamma_{11} - 1)^2 + \gamma_{12}^2)^3} \end{aligned} \quad (\text{S16})$$

For the discussion of v -representability, there are two common counterexamples: the first is a one-electron density with a certain type of cusp, given by Englisch and Englisch[1]; the other is a spherical p density related to a degeneracy that cannot be given by a single wavefunction[2]. The non- v -representable density matrices shown here are very different to these two examples and are only due to the nature of the energy surface of the exact functional as shown in Fig. S2.

B. Derivation of Löwdin-Shull for Hubbard model

Löwdin and Shull (LS) showed that the natural orbitals, ϕ_k , that diagonalize the density matrix and wavefunction for two electrons are the same

$$\Psi(\mathbf{r}, \mathbf{r}') = \sum_k c_k \phi_k(\mathbf{r}) \phi_k(\mathbf{r}') \quad (\text{S17})$$

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_k n_k \phi_k(\mathbf{r}) \phi_k(\mathbf{r}') \quad (\text{S18})$$

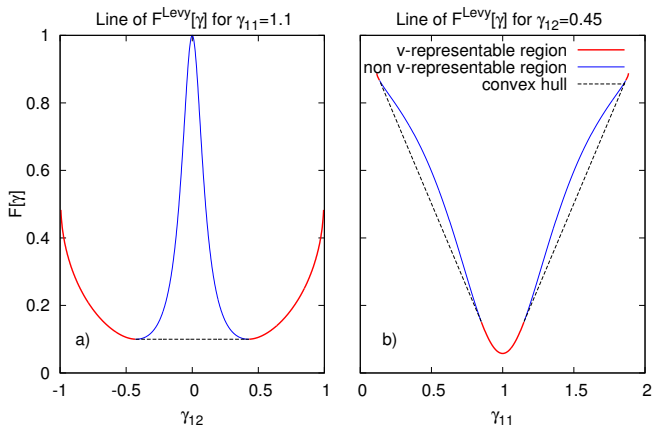


Figure S2: Two lines of $F^{\text{Levy}}[\gamma]$ that illustrate non- v -representable density matrices, due to the non convexity of the surface along the given line.

where $n_k = 2c_k^2$.

$$E^{\text{LS}}[\Psi] = \sum_{i=1}^2 c_i^2 \{2h_{ii} + \langle ii|ii \rangle\} + 2c_1c_2 \langle 11|22 \rangle \quad (\text{S19})$$

For two basis functions the minimum energy wavefunction comes from the coefficients of c_1 and c_2 having opposite signs, $c_1 = \sqrt{n_1/2}$ and $c_2 = -\sqrt{n_2/2}$. Substituting this into the energy expression for the wavefunction gives an expression in terms of the natural orbitals and the natural orbital occupation numbers, n_k ,

$$F^{\text{LS}}[\gamma] = \frac{1}{2}n_a \langle aa|aa \rangle + \frac{1}{2}n_b \langle bb|bb \rangle - \sqrt{n_a n_b} \langle aa|bb \rangle. \quad (\text{S20})$$

There has been some recent interest in natural orbitals [3] and natural orbital functionals that, for two electron

systems, must reduce to the Löwdin-Shull expression if they are to be exact, for example the PNOF5 functional [4–6].

The eigenvalues of the density matrix $\gamma = \begin{pmatrix} \gamma_{11} & \gamma_{12} \\ \gamma_{12} & 2 - \gamma_{11} \end{pmatrix}$ are

$$(\gamma_{11} - n)((2 - \gamma_{11} - n) - \gamma_{12}^2) = 0 \quad (\text{S21})$$

$$n^2 - 2n + 2\gamma_{11} - \gamma_{11}^2 - \gamma_{12}^2 = 0 \quad (\text{S22})$$

$$n_{\pm} = \left(-2 \pm \sqrt{4 - 4(\gamma_{11} - 1)^2 + 4\gamma_{12}^2} \right) / 2 \quad (\text{S23})$$

$$n_{\pm} = n_{a/b} = 1 \pm \sqrt{(\gamma_{11} - 1)^2 + \gamma_{12}^2}. \quad (\text{S24})$$

The $\langle pp|qq \rangle$ integrals are in the natural orbital basis and the coefficients of the natural orbitals (C_{pi}) are found by substituting in the natural orbital numbers e.g. $(\gamma_{11} - n_p)C_{p1} + \gamma_{12}C_{p2} = 0$ or (also using $C_{\pm i} = C_{(a/b)i}$)

$$C_{\pm 1} = \frac{(\gamma_{11} - 1) \pm \sqrt{(\gamma_{11} - 1)^2 + \gamma_{12}^2}}{\gamma_{12}} C_{\pm 2} \quad \text{and} \quad C_{\pm 1}^2 + C_{\pm 2}^2 = 1 \quad (\text{S25})$$

So overall, $C_{\pm 1}^2 = a_{\pm}^2 / (\gamma_{12}^2 + a_{\pm}^2)$ and $C_{\pm 2}^2 = \gamma_{12}^2 / (a_{\pm}^2 + \gamma_{12}^2)$ and hence

$$F^{\text{LS}} = \frac{1}{2}n_a (C_{a1}^4 + C_{a2}^4)U + \frac{1}{2}n_b (C_{b1}^4 + C_{b2}^4)U - \sqrt{n_a n_b} (C_{a1}^2 C_{b1}^2 + C_{a2}^2 C_{b2}^2)U. \quad (\text{S26})$$

For convenience, replace $r = (\gamma_{11} - 1)$ and $S = \sqrt{r^2 + \gamma_{12}^2}$, to obtain the following expression

$$F^{\text{LS}} = \frac{(1+S)}{2} \left[\left(\frac{(r+S)^2}{\gamma_{12}^2 + (r+S)^2} \right)^2 + \left(\frac{\gamma_{12}^2}{\gamma_{12}^2 + (r+S)^2} \right)^2 \right] + \frac{(1-S)}{2} \left[\left(\frac{(r-S)^2}{\gamma_{12}^2 + (r-S)^2} \right)^2 + \left(\frac{\gamma_{12}^2}{\gamma_{12}^2 + (r-S)^2} \right)^2 \right] - \sqrt{1-S^2} \left[\frac{(r+S)^2}{\gamma_{12}^2 + (r+S)^2} \frac{(r-S)^2}{\gamma_{12}^2 + (r-S)^2} + \frac{\gamma_{12}^2}{\gamma_{12}^2 + (r+S)^2} \frac{\gamma_{12}^2}{\gamma_{12}^2 + (r-S)^2} \right] \quad (\text{S27})$$

This equation could be simplified further but we have checked, by numerical evaluation with Fortran code, that it gives identical results to Eq. (13).

C. Complex

The constrained search $\Psi \rightarrow \gamma$ can be expanded over complex wavefunctions where the parameters, a, b, c , in the wavefunction

$$\Psi = \frac{a}{\sqrt{2}} [\mathcal{A}(\phi_1 \alpha \phi_2 \beta) + \mathcal{A}(\phi_2 \alpha \phi_1 \beta)]$$

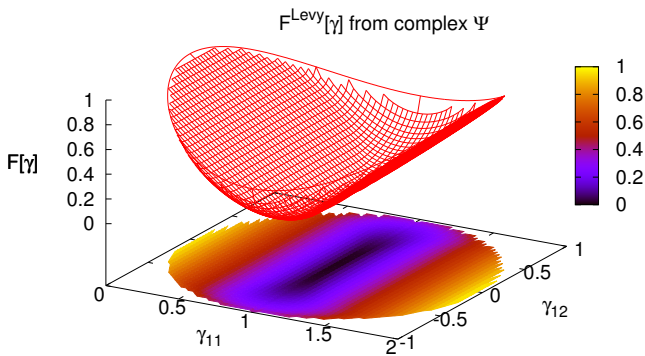


Figure S3: The exact functional allowing the wavefunction to be complex in the Levy search.

$$+b\mathcal{A}(\phi_1\alpha\phi_1\beta) + c\mathcal{A}(\phi_2\alpha\phi_2\beta) \quad (\text{S28})$$

are allowed to be complex

$$a = a_r + ia_i$$

$$b = b_r + ib_i$$

$$c = c_r + ic_i$$

In terms of these parameters there are the following constraints:

$$1 = a_r^2 + a_i^2 + b_r^2 + b_i^2 + c_r^2 + c_i^2$$

$$\gamma_{11} = 2a_r^2 + 2a_i^2 + b_r^2 + b_i^2$$

$$\Re(\gamma_{12}) = \sqrt{2}(a_r b_r + a_i b_i + b_r c_r + b_i c_i)$$

The imaginary part $\Im(\gamma_{12})$ can be anything as it does not enter the energy expression. A fourth constraint can be included if the overall phase of the wavefunction is set to zero.

We now carry out a search over all possible wavefunctions minimizing E and a given γ_{11} and $\Re(\gamma_{12})$, which gives Fig. S3. We do this by an explicit grid search over the two remaining variables for each γ_{11}, γ_{12} that is specified. The resulting energy functional gives the same result as the Hubbard expression Eq. (13) for all density matrices except the non- v -representable set. For all possible FCI density matrices it is, of course, in agreement with $F^{\text{HK}}[\gamma_v]$. For the non- v -representable set, $F_{\text{complex}}^{\text{Levy}}[\gamma]$ can be lower in energy, though this does not change any physics as these points can never be minima of any Hamiltonian. In this case, the functional numerically agrees with the ensemble functional considered by Saubèner and Pastor[7] given by a density matrix that is an ensemble of two wavefunctions $\Gamma = a|\Psi_a\rangle\langle\Psi_a| + b|\Psi_b\rangle\langle\Psi_b|$. It should be noted that when $F_{\text{complex}}^{\text{Levy}}[\gamma]$ is lower than Eq. (13) the solutions have a current and this may give a connection to the exact functional in current DFT (CDFT) [8, 9].

D. Lieb maximization

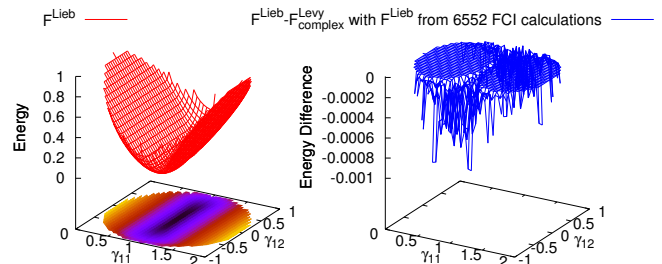


Figure S4: Functional $F^{\text{Lieb}}[\rho]$ from Lieb maximization using 6552 FCI calculations

Another way to calculate a bound for the functional is to perform the Lieb maximization[10],

$$F^{\text{Lieb}}[\gamma] = \sup_v \{E_v - \gamma.v\} \quad (\text{S29})$$

which is a supremum (a smallest upper bound which for any finite set would just be a maximum) on the set of v . This means for a finite set it would actually be a lower bound to the true minimum $F^{\text{Lieb}}[\gamma] \leq F^{\text{Levy}}[\gamma]$. The Lieb maximization is carried out using 6552 FCI calculations for v , with $-10 < t < 10$ and $-10 < \Delta\epsilon < 10$. Over a grid of density matrices, we compare directly with $F_{\text{complex}}^{\text{Levy}}$ from complex wavefunctions as in the region of non- v -representable densities it is closest to the complex or ensemble form. Carrying out the maximization of Eq. (S29) gives the results in the left hand side of Fig. S4 and the difference to $F_{\text{complex}}^{\text{Levy}}$ is shown in the right-hand side. This difference is small and negative which illustrates that the Lieb maximization only gives a lower bound to the true functional that in this case is known exactly. Obviously, with more and more FCI calculations F^{Lieb} would approach closer to the correct result. The $F^{\text{Lieb}}[\gamma]$ should not be used in minimizations in the same way as $F^{\text{Levy}}[\gamma]$ as it is a lower bound rather than an upper bound. Finally it should be noted that $F^{\text{Lieb}}[\gamma]$ is everywhere convex by construction and cannot, for example, contribute to the discussion on v -representability.

E. Approximate Density Matrix Functionals

We consider various approximate density matrix functionals including Hartree-Fock as a density matrix functional, Muller[11], Power [12]. Here the value of the natural orbital occupation numbers $0 \leq n_i \leq 2$ and the two-electron integrals $\langle pq|rs \rangle = \iint \phi_p^*(\mathbf{r})\phi_r(\mathbf{r})V_{ee}(\mathbf{r}, \mathbf{r}')\phi_q^*(\mathbf{r}')\phi_s(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$ which in the asymmetric two-site Hubbard model just work out to be $\langle pq|rs \rangle = \sum_{i=1,2} C_{pi}C_{qi}C_{ri}C_{si}$ in terms of the orbitals coefficients C_{pi} ($|p\rangle = \sum_{i=1,2} C_{pi}c_i^\dagger|\text{vac}\rangle$)

G. Functional for $N = 0, 1, 2, 3$ and 4

$$F^{\text{Hartree-Fock}} = \frac{1}{2}n_i n_j \langle ij | ij \rangle - \frac{1}{4}n_i n_j \langle ii | jj \rangle$$

$$F^{\text{Müller}} = \frac{1}{2}n_i n_j \langle ij | ij \rangle - \frac{1}{2}\sqrt{n_i n_j} \langle ii | jj \rangle$$

$$F^{\text{Power}} = \frac{1}{2}n_i n_j \langle ij | ij \rangle - \frac{1}{2}(n_i n_j)^\alpha \langle ii | jj \rangle$$

In the paper we use a value $\alpha = 0.675$ that has recently been used for Mott insulators

F. Gutzwiller approximate wavefunction

The Gutzwiller wavefunction [13] is a parametrized wavefunction of the form

$$\Psi = \frac{1}{\sqrt{2}} [\mathcal{A}(\phi_1 \alpha \phi_2 \beta) + \mathcal{A}(\phi_2 \alpha \phi_1 \beta)] + g [\mathcal{A}(\phi_1 \alpha \phi_1 \beta) + \mathcal{A}(\phi_2 \alpha \phi_2 \beta)]$$

When $g = 1$ it is the Hartree-Fock wavefunction for orbitals $\phi = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$. The basic idea is that in an H_2 like system as $g \rightarrow 0$ it goes to the Heitler-London wavefunction. In the asymmetric two-site Hubbard model we consider an orbital of the form $\phi = c_1 \phi_1 + \sqrt{1 - c_1^2} \phi_2$ and a Gutzwiller wavefunction

$$\Psi^{\text{GWA}} = \frac{2c_1 \sqrt{1 - c_1^2}}{\sqrt{2}} [\mathcal{A}(\phi_1 \alpha \phi_2 \beta) + \mathcal{A}(\phi_2 \alpha \phi_1 \beta)] + g [c_1^2 \mathcal{A}(\phi_1 \alpha \phi_1 \beta) + (1 - c_1^2) \mathcal{A}(\phi_2 \alpha \phi_2 \beta)]$$

If we consider all possible values of c_1 and $-1 \leq g \leq 1$ we get the following density matrices and

$$F[\Psi^{\text{GWA}}] = \frac{\langle \Psi^{\text{GWA}} | V_{ee} | \Psi^{\text{GWA}} \rangle}{\langle \Psi^{\text{GWA}} | \Psi^{\text{GWA}} \rangle}.$$

For other values of $|g| > 1$ the wavefunction is no longer a ground state wavefunction.

The functional is calculated for different integer numbers of electrons ($N = 0, 1, 2, 3$ and 4), where the trace of the density matrix $\gamma_{11} + \gamma_{22} = N$. At $N = 0$, $F[\gamma] = 0$ and there is only one allowed density matrix $\gamma_{11} = \gamma_{12} = 0$. For $N = 1$, $F[\gamma] = 0$ as there is no electron-electron interaction, however, the allowable density matrices from a pure state wavefunction are now defined by a circle $\gamma_{12} = \sqrt{(\gamma_{11} - 0.5)^2 - 0.5^2}$. Inside this circle are ensemble- N -representable density matrices but

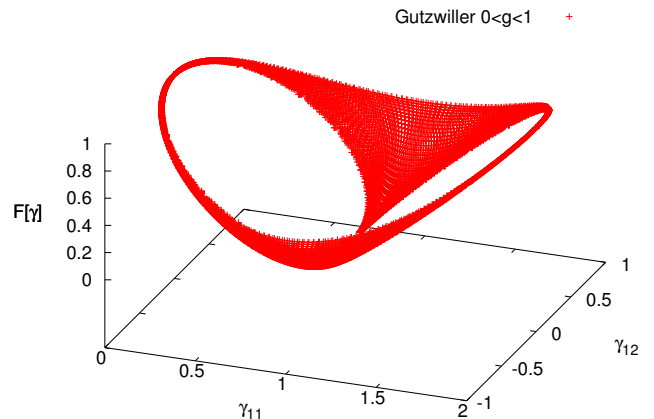


Figure S5:

they cannot come from a pure-state wavefunction. For $N = 2$, $F[\gamma]$ is that of Eq. (13). For $N = 3$, $F[\gamma] = 1$ at the allowed pure-state density matrices defined by a different circle $\gamma_{12} = \sqrt{(\gamma_{11} - 1.5)^2 - 0.5^2}$. Also at $N = 4$, $F[\gamma] = 2$ at density matrix $\gamma_{11} = 2$, $\gamma_{12} = 0$. All these integer parts of the exact functional are pictured in the supplementary information.S6

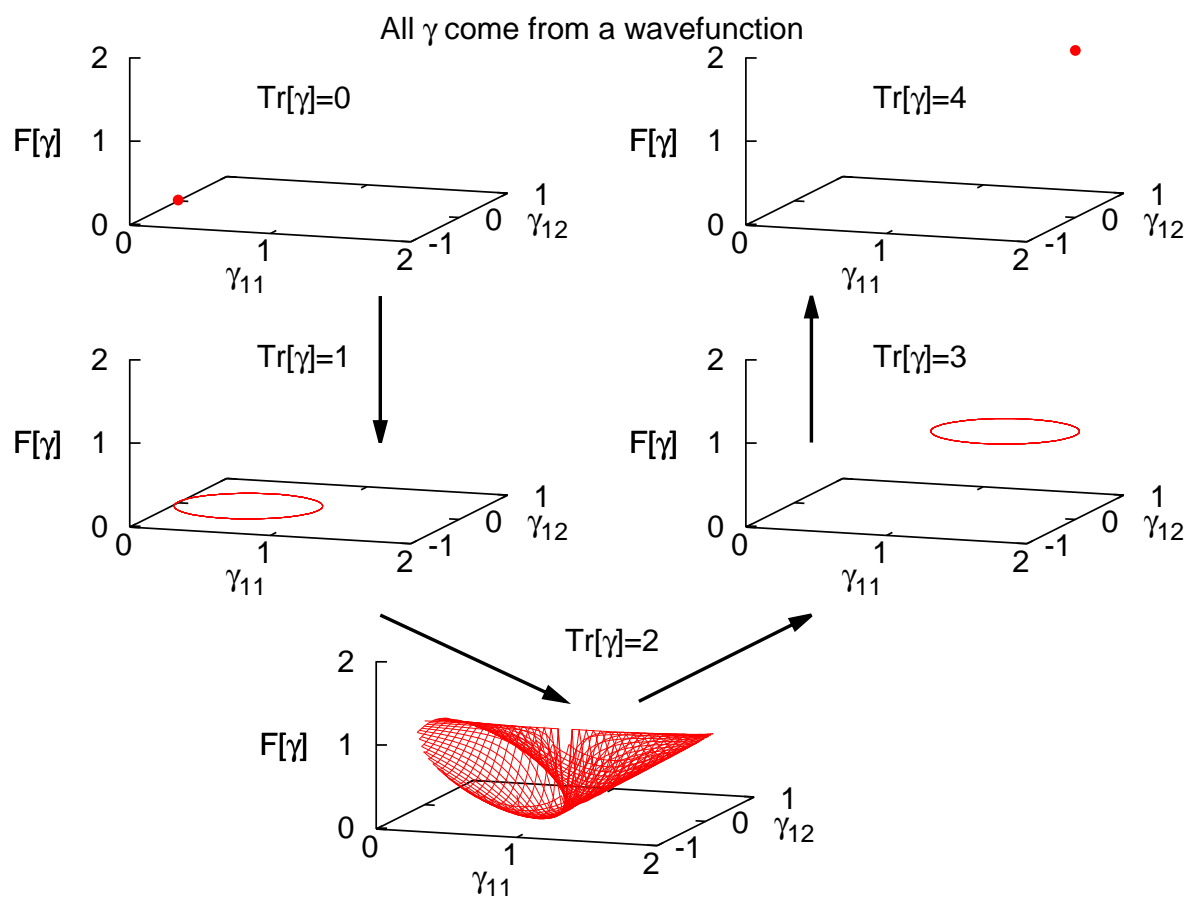


Figure S6: $F[\gamma]$ for $N = 0, 1, 2, 3, 4$ electrons

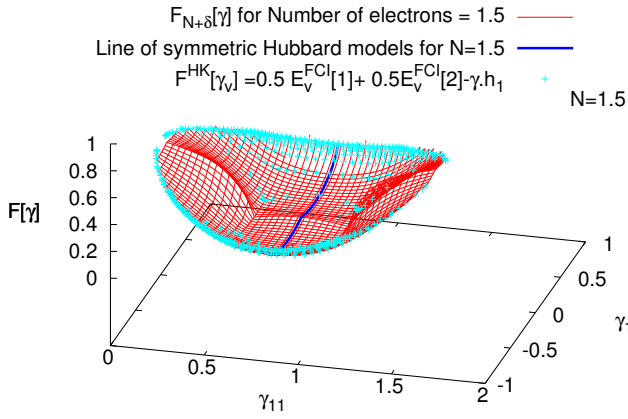


Figure S7: The exact functionals of Eqs (S30) and (S31) for $N = 1.5$ electrons, which gives back the exact energy of every system with 1.5 electrons.

H. Exact functional for $N = 1.5$ electrons

The exact functional for fractional number of electrons ($N + \delta$) from Perdew, Parr, Levy and Balduz is given by a constrained search over density matrices

$$F_{N+\delta}[\gamma] = \min_{\Gamma_{N+\delta} \rightarrow \gamma} \text{Tr}[\Gamma_{N+\delta} V_{ee}], \quad (\text{S30})$$

The Hohenberg-Kohn version of the fractional exact functional can be calculated from the linear combination of FCI energies at N and $N + 1$

$$F_{N+\delta}^{\text{HK}}[v] = (1 - \delta)E_v^{\text{FCI}}[N] + \delta E_v^{\text{FCI}}[N + 1] - [(1 - \delta)\gamma_v^N + \delta\gamma_v^{N+1}] \cdot v \quad (\text{S31})$$

In the consideration of fractional numbers of electrons

the argument of convexity of E vs N is often used to simplify the ensembles that have to be taken.

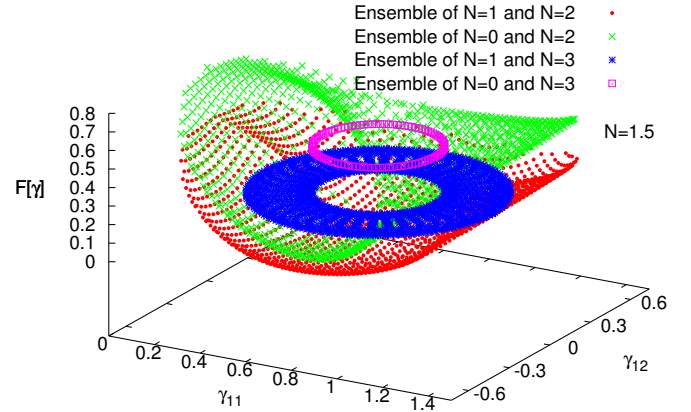


Figure S8: Different ensemble formation of $F[\gamma^{N=1.5}]$ combining pure state wavefunction for $N = 0, 1, 2, 3$ electrons

If convexity is true, the lowest energy ensemble will always be given by the combination of the two integers at either side, e.g. $\Gamma_{N+\delta} = (1 - \delta)\Gamma_N + \delta\Gamma_{N+1}$. However, convexity has not been proven, with definitely known counterexamples for certain electron-electron interactions, which indicates that most certainly convexity is not a general property of Hamiltonians [10]. Here, we test convexity for the two-site Hubbard hamiltonians, by taking ensembles of different electron numbers. We consider different pair-wise ensembles $\Gamma_{N=1.5} = a|\Psi_{n_1}\rangle\langle\Psi_{n_1}| + b|\Psi_{n_2}\rangle\langle\Psi_{n_2}|$ with $\{n_1, n_2\} = \{1, 2\}, \{0, 2\}, \{1, 3\}, \{0, 3\}$. We have also considered all possible ensembles, including those of three and four different particle numbers up to $N = 4$, all of these lie higher in energy.

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