

The connection between wave function theory and density-functional theory in the asymmetric Hubbard dimer

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Exact Hamiltonian for singlet states

We consider the Hamiltonian $\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}$ of the asymmetric Hubbard dimer in the **site basis**:

$$\begin{array}{cccc} |1 \uparrow 1 \downarrow\rangle & |1 \uparrow 2 \downarrow\rangle & |1 \downarrow 2 \uparrow\rangle & |2 \uparrow 2 \downarrow\rangle \\ \uparrow\downarrow \cdot & \uparrow \downarrow & \downarrow \uparrow & \cdot \uparrow\downarrow \end{array}$$

$$\mathbf{H} = \begin{pmatrix} -\Delta v + U & -t & t & 0 \\ -t & 0 & 0 & t \\ t & 0 & 0 & -t \\ 0 & t & -t & \Delta v + U \end{pmatrix}$$

- t is the hopping parameter
- U is the on-site Coulomb repulsion
- $\Delta v = v_2 - v_1$ is the difference of on-site potentials

In the site basis, one can write the **exact wave function** as

$$\Psi = \beta_1 |1 \uparrow 1 \downarrow\rangle + \alpha (|1 \uparrow 2 \downarrow\rangle + |1 \downarrow 2 \uparrow\rangle) + \beta_2 |2 \uparrow 2 \downarrow\rangle$$

with $2\alpha^2 + \beta_1^2 + \beta_2^2 = 1$ (normalization condition). The energy can be written as

$$E(\alpha, \beta_1, \beta_2) = T(\alpha, \beta_1, \beta_2) + V_{ee}(\alpha, \beta_1, \beta_2) + V(\alpha, \beta_1, \beta_2)$$

with

$$T(\alpha, \beta_1, \beta_2) = -4t\alpha(\beta_1 + \beta_2)$$

$$V_{ee}(\alpha, \beta_1, \beta_2) = U(\beta_1^2 + \beta_2^2)$$

$$V(\alpha, \beta_1, \beta_2) = -\Delta v(\beta_1^2 - \beta_2^2)$$

NB: One can obtain analytically the energies and wave function coefficients

Let us introduce the **site occupation difference**

$$\Delta n = n_2 - n_1$$

- n_1 is the occupation of site 1
- n_2 is the occupation of site 2
- Δn plays the role of the density (**site-occupation function theory**)

Let us assume that we know the **universal Hohenberg-Kohn functional** $F(\Delta n)$ such that

$$E(\Delta n_0) = F(\Delta n_0) + V(\Delta n_0) = F(\Delta n_0) + \Delta v \Delta n_0 / 2$$

is the exact **ground-state** energy of the system for a given Δv

The minimizing Δn is obtained by solving the following Euler equation

Find Δn_0 such that $\left. \frac{\partial E(\Delta n)}{\partial \Delta n} \right _{\Delta n = \Delta n_0} = 0 \quad \Leftrightarrow \quad \left. \frac{\partial F(\Delta n)}{\partial \Delta n} \right _{\Delta n = \Delta n_0} = -\Delta v / 2$

Hohenberg & Kohn, Phys. Rev. 136 (1964) B864

Non-interacting kinetic energy functional:

$$T_s(\Delta n) = -2t \sqrt{\left(1 - \frac{\Delta n}{2}\right) \left(1 + \frac{\Delta n}{2}\right)}$$

Hartree-exchange functional:

$$E_{\text{Hx}}(\Delta n) = \frac{U}{2} \left[1 + \left(\frac{\Delta n}{2}\right)^2 \right]$$

Correlation functional:

$$F_c(\Delta n) = F(\Delta n) - T_s(\Delta n) - E_{\text{Hx}}(\Delta n)$$

Kohn & Sham, Phys. Rev. 140 (1965) A1133

Connection between wave function and density worlds

The equation connecting the WFT and DFT worlds is

$$\Delta n = n_2 - n_1 = 2(\beta_2^2 - \beta_1^2)$$

Let us construct the universal functional via the **Levy-Lieb constrained search** approach:

$$F(\Delta n) = \min_{\Psi \rightarrow \Delta n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

The ground-state energy is determined by a second minimization step:

$$E(\Delta n_0) = \min_{\Delta n} E(\Delta n) = \min_{\Delta n} \{F(\Delta n) + \Delta v \Delta n / 2\}$$

Levy, PNAS 76 (1979) 6062; Lieb, IJQC 24 (1983) 243

$F(\Delta n)$ for the Hubbard dimer (1)

By definition, $F(\Delta n)$ is given by

$$\begin{aligned} F(\Delta n) &= \min_{\substack{\alpha, \beta_1, \beta_2 \\ 2\alpha^2 + \beta_1^2 + \beta_2^2 = 1 \wedge \Delta n = \beta_2^2 - \beta_1^2}} [T(\alpha, \beta_1, \beta_2) + V_{ee}(\alpha, \beta_1, \beta_2)] \\ &= \min_{\substack{\alpha, \beta_1, \beta_2 \\ 2\alpha^2 + \beta_1^2 + \beta_2^2 = 1 \wedge \Delta n = \beta_2^2 - \beta_1^2}} [-4t\alpha(\beta_1 + \beta_2) + U(\beta_1^2 + \beta_2^2)] \end{aligned}$$

By defining $g = \alpha(\beta_1 + \beta_2)$ and $\rho = |\Delta n|/2$, we obtain

$$F(\rho) = \min_g f(g, \rho)$$

with

$$f(g, \rho) = -2tg + U \frac{g^2(1 - \sqrt{1 - g^2 - \rho^2}) + 2\rho^2}{2(g^2 + \rho^2)}$$

Let us find $g_0(\rho)$ such that

$$\left. \frac{\partial f(g, \rho)}{\partial g} \right|_{g=g_0(\rho)} = 0$$

$g_0(\rho)$ is one of the solution of the following sixth-order polynomial [$u = U/(2t)$]:

$$g^4 (\rho^2 (u^2 + 3) - 1) + g^2 \rho^2 (\rho^2 (u^2 + 3) - u^2 - 2) + \frac{1}{4} g^6 (u^2 + 4) \\ + 2g^3 \rho^2 u - 2g\rho^2 (1 - \rho^2) u - \rho^4 (1 - \rho^2) = 0$$

If you can find analytically $g_0(\rho)$, you'll be able to get the exact functional for the asymmetric Hubbard dimer, i.e., $F(\rho, g_0(\rho))$

Other options are available:

- $f = \beta_1^2 + \beta_2^2$ and $\rho = |\Delta n|/2$
 - $\Rightarrow f_2(f, \rho) = -2t\sqrt{1-f}(\sqrt{f+\rho} - \sqrt{f-\rho} + Uf)$
 - \Rightarrow Sixth-order polynomial in f
- $l = (\beta_1 + \beta_2)^2$ and $\rho = |\Delta n|/2$
 - $\Rightarrow f_3(l, \rho) = -2t\sqrt{2l - l^2 - \rho^2} + U\frac{l^2 + \rho^2}{2l}$
 - \Rightarrow Sixth-order polynomial in l
- $x = ?$ and $\rho = |\Delta n|/2 \Rightarrow f_4(x, \rho) = \text{simple function}$
 - \Rightarrow Nice-order polynomial in $x \Rightarrow$ **Closed form!**



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