Strongly correlated systems and the dissociation-limit Kohn-Sham potential

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Motivation

- Common exchange-correlation functionals do not account well for strongly correlated systems
- A notable example is the stretching and dissociation of H_2
- This talk is about the physics and Kohn-Sham potential of H_2-like systems in the dissociation limit, revealing some fundamental features of the True Functional

Paper reference

- N. Helbig, I.V. Tokatly, A. Rubio: "Exact Kohn-Sham potential of strongly correlated finite systems"
- (I suppose you could say that the part about "finite" may be a bit of a *stretch*, so to speak)
- arXiv:0908.0710v1 [cond-mat.str-el] 5 Aug 2009

What happens in the paper/talk

- We consider two-atom, two-electron systems in the dissociation limit
- For sufficiently simple systems it is possible to get the exact Kohn-Sham potential, which yields a correct description in the dissociation limit

The hydrogen molecule in reality

- The H_2 ground state is the ordinary bonding orbital occupied with one electron of each spin
- This is a singlet state: spatial part is symmetric, spin part antisymmetric $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$
- In other words: the electrons have opposite spin, and reside equally on each atom. Both spins thus contribute equally to the electron density everywhere.
- As the molecule dissociates, eventually we must end up with two single hydrogen atoms, each with one electron possessing a definite spin (a triplet state)
- I.e. the electrons each reside on one atom. The density around each atom is either completely spin-up or spin-down.

Hubbard model

- Consider the Hubbard Hamiltonian ($c_{i\sigma}$ removes an electron on atom i with spin σ):

$$H = -t \sum_{\sigma} (c^{\dagger}_{1\sigma} c_{2\sigma} + \mathrm{etc.}) + U \sum_{i} c^{\dagger}_{i\downarrow} c_{i\downarrow} c^{\dagger}_{i\uparrow} c_{i\uparrow}$$

- The Hubbard term adds energy for having both spin states occupied on the same atom
- In the dissociation limit, $t \to 0$ (no hopping), and the U contribution will dominate, penalizing mixed spins and recovering correct ground state with electrons localized on distinct atoms

Symmetry breaking

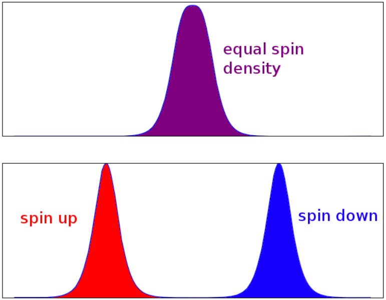


Figure: Neutral spin-density of two electrons with same spatial wavefunction (top) versus separate spin-polarized densities of isolated atoms (below). Shapes and scales are arbitrary

The hydrogen molecule in Kohn-Sham

- Normal functionals describe ground state of H_2 well but fail to reproduce symmetry break for large atomic separations
- The Kohn-Sham electrons are non-interacting, and thus cannot "talk together" to localize on distinct atoms. Thus there must be a KS orbital residing on both atoms, which is the true KS ground state
- But if DFT is supposed to be exact, then there must exist a true Kohn-Sham potential that yields the correct total density anyway

Some basic equations

- Suppose we have a Kohn-Sham state $\phi(\mathbf{r})$ with two electrons in it. Then the density is

$$n(\mathbf{r}) = 2|\phi(\mathbf{r})|^2 = 2\phi^2(\mathbf{r})$$

- The Kohn-Sham equation for this state is

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi(\mathbf{r}) = \epsilon\phi(\mathbf{r})$$

- Isolating the Kohn-Sham potential, and substituting $n(\mathbf{r})$,

$$v_s(\mathbf{r}) = \frac{1}{2}\frac{\nabla^2\sqrt{n(\mathbf{r})}}{\sqrt{n(\mathbf{r})}} + \epsilon$$

We can get the KS potential for any density like that.

Extremely simple 1D system

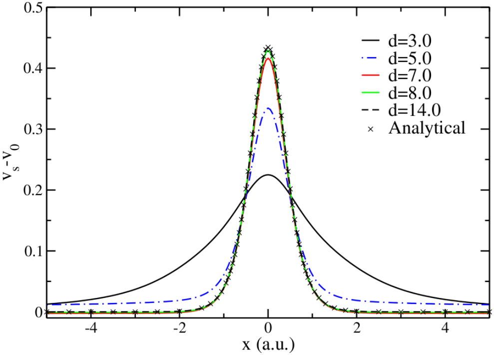
- Atomic potential: $v_{\text{ext}}(x) = -v\left[\delta(x - \frac{d}{2}) + \delta(x + \frac{d}{2})\right]$
- Interaction potential: $v_{\text{int}}(|x - x'|) = \lambda\delta(x - x'), \quad \lambda \to \infty$
- This can be solved analytically

Solutions

- Wavefunction $\Psi(x, x') = |\phi_+(x)\phi_-(x') - \phi_+(x')\phi_-(x)|$, with $\phi_\pm(x) = e^{-\alpha_\pm|x+d/2|} \pm e^{-\alpha_\pm|x-d/2|}$
- Density $n(x) = \phi_+^2(x) + \phi_-^2(x)$
- This density corresponds to the KS potential (for $d \to \infty$): $v_s(x) = v_{\text{ext}}(x) + \Delta v_s(x), \quad \Delta v_s(x) = \frac{v^2}{2\cosh^2(2vx)}$
- The potential $\Delta v_s(x)$ is shaped like a wall between the atoms, even though the atoms are very far away!

Slightly more complicated 1D system

- $v_{\text{ext}}(x) = -v\left[\frac{1}{\cosh^2(x-d/2)} + \frac{1}{\cosh^2(x+d/2)}\right]$
- $v_{\text{int}}(|x-x'|) = \frac{b}{\cosh^2(x-x')}$



From numerically calculated WFs, the Kohn-Sham potential $\Delta v_s(x)$ approaches the same shape as the previous analytical wall in spite of the different form of v_{ext} and v_{int}. Apparently this shape is somehow universal!

Some remarks

- As we know, the KS system cannot possibly break the symmetry, and is stuck with an orbital that covers both atoms
- The exact KS potential takes the shape of a wall between the atoms, forcing the orbital to reproduce the separate atomic densities
- This prevents "hopping" between the atoms, much like what takes place in the Hubbard model.
- The wall is evidently a fundamental physical feature, which doesn't depend on the exact shape of the potentials v_{ext} and v_{int}. However it does depend on the well depth v, or ionization potential $I = -v^2/2$

Asymmetric dimers

- Consider the asymmetric external potential $v_{\text{ext}} = -\frac{v_1}{\cosh^2(x-d/2)} - \frac{v_2}{\cosh^2(x+d/2)}$
- The exact KS potential now contains two contributions ($\alpha_{1,2}$ and $I_{1,2}$ simply related to $v_{1,2}$)

$$v_s^{(1)}(x) = \frac{(\alpha_1+\alpha_2)^2/8}{\cosh^2[(\alpha_1+\alpha_2)(x+x_0)]} \quad \text{“wall”}$$

$$v_s^{(2)}(x) = \frac{I_2 - I_1}{1+\exp[2(\alpha_1+\alpha_2)(x+x_0)]} \quad \text{“shelf”}$$

with $x_0 = \mathcal{O}(d)$

- Aside from the wall, the potential on one side of the wall is shifted so as to make the atomic potential wells equally deep

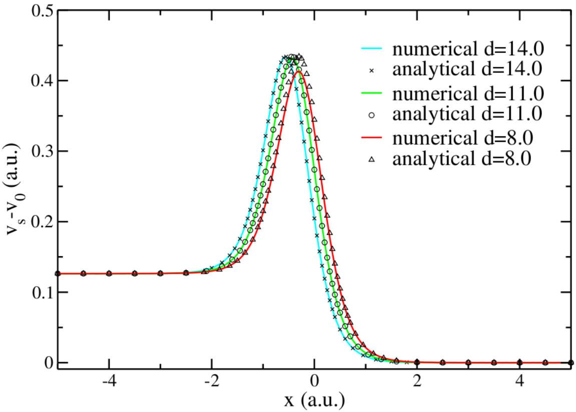


Figure: Shell plus wall appearing for different atom types. The potential eventually approaches zero for $x \to -\infty$

3D systems

- The formula for the exact KS potential from the density can be readily generalized to 3D. Thus it is trivial to perform a numerical calculation on a real (dissociated) H_2 system.
- The exact KS potential is

$$\Delta v_s^{\mathrm{H}_2}(\mathbf{r}) = \frac{1 - \mathbf{r}_1 \cdot \mathbf{r}_2 / r_1 r_2}{4\cosh^2(r_2 - r_1)}$$

- This has the form of a peak as seen previously with the same functional form along the molecular axis

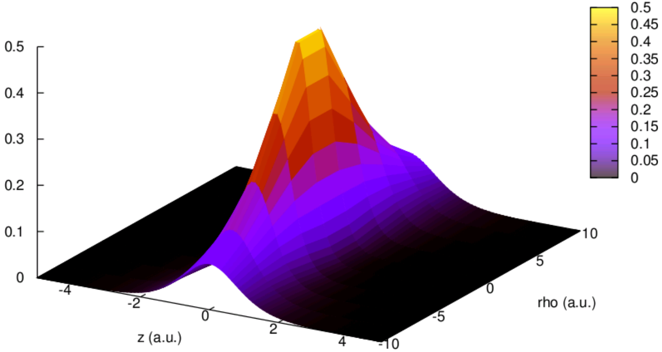


Figure: Kohn-Sham potential for H_2 in the dissociation limit

Conclusion

- The Kohn-Sham potential of any two-electron system can be calculated in the dissociation limit
- The potential depends only on the ionization potentials of the atoms in question; aside from these, its form is universal
- Maybe some day, all this can be included in standard XC approximations!