

Wigner density functional theory and the lowest excited configuration of Harmonium

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In general we deal with the nonrelativistic QM of an **electronic system**, to wit,

$$H = \mathbf{T} + \mathbf{V}_{\text{ext}} + \mathbf{V}_{\text{ee}} = \sum_{i=1}^N -\frac{1}{2}\Delta_{\vec{q}_i} + \sum_{i=1}^N V(\vec{q}) + \sum_{i<j}^N \frac{1}{|\vec{q}_i - \vec{q}_j|}.$$

Pure states $D_N = |\psi\rangle\langle\psi|$ have **skewsymmetric** $\psi(x_1, \dots, x_N)$, with $x_i = (\vec{q}_i, \varsigma_i)$, spatial and spin variables.

Integrating out x_3, \dots, x_N gives a **reduced 2-matrix**:

$$D_2(x_1, x_2; x'_1, x'_2) = \int D_N(x_1, x_2, x_3, \dots, x_N; x'_1, x'_2, x_3, \dots, x_N) dx_3 \dots dx_N.$$

We can integrate further to get the **reduced 1-matrix**

$$D_1(x; x') = \int D_2(x, x_2; x', x_2) dx_2.$$

Let now think of ions. There is the helium-like energy functional:

$$\mathcal{E}(D_2) = N \operatorname{Tr} \left[\left(-\frac{\Delta_{\vec{q}_1}}{2} - \frac{Z}{|\vec{q}_1|} \right) D_2 \right] + \frac{N(N-1)}{2} \operatorname{Tr} \left[\left(\frac{1}{|\vec{q}_1 - \vec{q}_2|} \right) D_2 \right].$$

The **ground-state energy** minimizes $\mathcal{E}(D_2)$; but over what set of 2-matrices, we do not know. This is the **N-representability problem**. The set of **admissible 1-matrices** is indeed known [Coleman 1963]: $D_1 \geq 0$, $\operatorname{Tr} D_1 = 1$ and all its eigenvalues obey $0 \leq \lambda \leq 1/N$. It is a convex set and its extremal states are those coming from **Hartree-Fock** states.

The **electronic density** comes from the diagonal summed over the spin states

$$\rho(\vec{q}) := N \sum_{\varsigma} D_1(\vec{q}, \varsigma; \vec{q}, \varsigma).$$

This is **the** variable in Kohn's DFT.

It is clear that much information about the system depends on ρ only. For instance, the **Thomas-Fermi theory** approximates the kinetic energy as the functional

$$T_{\text{TF}}[\rho] = C_F \int \rho^{5/3}(\vec{q}) d\vec{q},$$

with $C_F = 2.871$.

Henceforth when possible we replace D_N by a phase-space function

$$P_N(\mathbf{q}; \mathbf{p}) \equiv P_N(\vec{q}_1, \dots, \vec{q}_N; \vec{p}_1, \dots, \vec{p}_N),$$

omitting spin indices for simplicity. This is the **Wigner function** for $|\psi\rangle\langle\psi|$:

$$P_N(\mathbf{q}; \mathbf{p}) := \pi^{-3N} \int D_N(\mathbf{q} - \mathbf{z}; \mathbf{q} + \mathbf{z}) e^{2i\mathbf{p}\cdot\mathbf{z}} d\mathbf{z}_1 \dots d\mathbf{z}_N.$$

This is a real function and $\text{Tr } D_N = 1$ becomes $\int P_N(\mathbf{q}; \mathbf{p}) = 1$.
However P_N can take **some negative values**.

One can also model **transitions** $|\psi\rangle\langle\phi|$:

$$P_{\psi\phi}(\mathbf{q}; \mathbf{p}) := \pi^{-3N} \int \psi(\mathbf{q} - \mathbf{z}) \phi^*(\mathbf{q} + \mathbf{z}) e^{2i\mathbf{p}\cdot\mathbf{z}} d\mathbf{z}_1 \dots d\mathbf{z}_N.$$

In WDFT D_2 and D_1 are replaced by **quasidensities**:

$$d_2(\vec{q}_1, \vec{q}_2; \vec{p}_1, \vec{p}_2) = \binom{N}{2} \int P_N(q; p) d\vec{q}_3 \dots d\vec{q}_N d\vec{p}_3 \dots d\vec{p}_N,$$

$$d(\vec{q}; \vec{p}) = N \int P_N(q; p) d\vec{q}_2 \dots d\vec{q}_N d\vec{p}_2 \dots d\vec{p}_N.$$

With these normalizations $\rho(\vec{q}) = \int d(\vec{q}; \vec{p}) d\vec{p}$.

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Operator products $FG \longleftrightarrow$ **Moyal products** $f \star g$. They obey

$$(f \star g)(\vec{q}; \vec{p}) = \pi^{-6N} \int f(\vec{q}'; \vec{p}') g(\vec{q}''; \vec{p}'') e^{2i(y^T A y' + y'^T A y'' + y''^T A y)} dy' dy'',$$

where $y := (\vec{q}, \vec{p})$ and $A = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$. We get:

$$\int (f \star g)(\vec{q}; \vec{p}) d\vec{q} d\vec{p} = \int f(\vec{q}; \vec{p}) g(\vec{q}; \vec{p}) d\vec{q} d\vec{p}.$$

Spectral theory works fine in the Moyal product notation. Assume that H has purely discrete, nondegenerate spectrum, $E_0 < E_1 < \dots < E_n < \dots$. One solves the eigenvalue equations

$$H \star \Gamma_{nm} = E_n \Gamma_{nm} \quad \text{and} \quad \Gamma_{nm} \star H = E_m \Gamma_{nm}$$

to get an orthonormal basis of **states** Γ_{mm} and **transitions** Γ_{nm} on phase space, obeying $\Gamma_{mn} \star \Gamma_{rs} = \delta_{nr} \Gamma_{ms}$.

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Then $H = \sum_n E_n \Gamma_{nn}$, so the variational principle reads now:

$$E_0 \leq \int H(q; p) P_N(q; p) dq dp$$

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HK-type theorem: The ground state quasidensity $d_{\text{gs}}(\vec{q}; \vec{p})$ determines the many-body ground state.

The quasidensity d can be written as

$$d(\vec{q}; \vec{p}) = \sum_{r \geq 0} n_r f_{rr}(\vec{q}; \vec{p}),$$

where the f_{rr} are orthonormal, $\sum_{r \geq 0} n_r = N$ and $0 \leq n_r \leq 1$ by Coleman's theorem: the n_r are the **occupation numbers**.

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The Wigner **natural orbitals** $f_{rr} \longleftrightarrow |\phi_r\rangle\langle\phi_r|$ are part of an orthonormal basis, including **transitions** $f_{rs} \longleftrightarrow |\phi_r\rangle\langle\phi_s|$, such that $f_{jk} \star f_{rs} = \delta_{kr} f_{js}$ and

$$d \star f_{rs} = n_r f_{rs} \quad \text{and} \quad f_{rs} \star d = n_s f_{rs}.$$

For two-electron systems, like H^- , He , Li^+ and H_2 , one can say more. There are **singlet** states,

$$\psi(x_1, x_2) = 2^{-1/2}(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)\phi(\vec{q}_1, \vec{q}_2)$$

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$$d_2(\vec{q}_1, \vec{q}_2; \vec{p}_1, \vec{p}_2) = \sum_{r,s \geq 0} c_r c_s f_{rs}(\vec{q}_1; \vec{p}_1) f_{rs}(\vec{q}_2; \vec{p}_2),$$

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in a **suitable basis** of natural Wigner orbitals/transitions f_{rs} . Since $\int f_{rs} d\vec{q} d\vec{p} = \delta_{rs}$ we get $d = \sum_{r \geq 0} c_r^2 f_{rr}(\vec{q}; \vec{p})$, and thus $c_r^2 = n_r$.

This means that d_2 could be recovered from d once we know the basis $\{f_{rs}\}$, if only we knew the signs of $c_r = \pm\sqrt{n_r}$. This is the **phase dilemma** [Löwdin-Shull 1956, Kutzelnigg 1963].

Let us abbreviate $f_{rs}(\vec{q}) = \int f_{rs}(\vec{q}; \vec{p}) d\vec{p}$. The contribution of f_{rs} to the interaction energy is

$$L_{rs} := \int \frac{f_{rs}(\vec{q}_1) f_{rs}(\vec{q}_2)}{|\vec{q}_1 - \vec{q}_2|} d\vec{q}_1 d\vec{q}_2.$$

The **Shull-Löwdin-Kutzelnigg (SKL) functional** for 2-electron systems (singlet case) is then

$$A[d] = \sum_{r,s \geq 0} c_r c_s L_{rs} = \sum_{r,s \geq 0} \pm\sqrt{n_r} \sqrt{n_s} L_{rs}.$$

The point is that for the **correct choice** of signs, this is **exact**. We take $c_1 = +\sqrt{n_1}$ for free. For ions, a good empirical choice is then $c_r = -\sqrt{n_r}$ for $r > 1$ [Shull-Löwdin, 1959].

The interaction energy functional $\mathcal{A}[d]$ for closed-shell systems can be approximated by one of the form *Coulomb* + *Exchange*:

$$\mathcal{A}[d] = \frac{1}{2} \int \frac{\rho(q_1)\rho(q_2)}{|q_1 - q_2|} d\vec{q}_1 d\vec{q}_2 - \sum_{r,s \geq 0} g_{rs} \int \frac{f_{rs}(\vec{q}_1)f_{rs}(\vec{q}_2)}{|q_1 - q_2|} d\vec{q}_1 d\vec{q}_2.$$

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[Frank, Lieb, Seiringer and Siedentop, 2007] shows that the new estimate satisfies $\mathcal{A}^M[d] < \mathcal{A}[d]$.

With the purpose of calibrating correlation energy, Moshinsky (1968) introduced a completely integrable analogue of a two-electron atom, here called *harmonium*. It describes two fermions interacting with an external harmonic potential and repelling each other by a Hooke-type force; thus the harmonium Hamiltonian in Hartree-like units is

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$$H = \frac{p_1^2}{2} + \frac{p_2^2}{2} + \frac{k}{2}(r_1^2 + r_2^2) - \frac{\delta}{4}|r_1 - r_2|^2.$$

It is worth saying that this model appears at the beginning of Quantum Mechanics [W. Heisenberg, Z. Physic. **38** 411 (1926)].

The “harmonium model” (or “Moshinsky atom”) is usually regarded as an exactly solvable laboratory bench for quantum chemistry. In the last few years, the model has been used extensively to study electronic **correlation**, approximation of **functionals** and questions of **entanglement**. The pioneer paper was by Srednicki, to argue about **black hole entropy** (1993).

Something **fun**: Müller’s functional gives **exactly the same result** for the energy on the “true” states as the exact one (for the ground state).

Using the **extracule**

$$\mathbf{R} = \frac{1}{\sqrt{2}}(\mathbf{r}_1 + \mathbf{r}_2)$$

and **intracule**

$$\mathbf{r} = \frac{1}{\sqrt{2}}(\mathbf{r}_1 - \mathbf{r}_2)$$

we get two independent oscillators:

$$H = H_R + H_r := \frac{p^2}{2} + \frac{\omega^2 R^2}{2} + \frac{p^2}{2} + \frac{\mu^2 r^2}{2}.$$

Here $\omega := \sqrt{k}$ and $\mu := \sqrt{k - \delta}$. Assume $\delta < k$.

The energy spectrum for **harmonium** is

$$\left(\mathbb{N} + \frac{3}{2}\right)\omega + \left(\mathbb{N} + \frac{3}{2}\right)\mu.$$

Since $\mu < \omega$, the energy of the first excited configurations is: $E_{fs} = (3\omega + 5\mu)/2$. For our present purposes, it is enough to choose an intracule excitation state along the x -axis (say). The corresponding 2-quasidensity is given by:

$$\frac{1}{\pi^6} \exp\left(-\frac{2H_R}{\omega}\right) \exp\left(-\frac{2H_r}{\mu}\right)$$

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$$\frac{2}{\pi^6} \exp\left(-\frac{2H_R}{\omega}\right) \exp\left(-\frac{2H_r}{\mu}\right) \left(\frac{(p_{1x} - p_{2x})^2 + \mu^2(x_1^2 - x_2^2)^2}{\mu} - \frac{1}{2}\right).$$

Henceforth we work in the chosen nontrivial mode, since the problem factorizes completely. By integrating one set of variables, the reduced one-body spinless quasidensity is obtained:

$$d(r; p) = 2 \int d_2(r, r_2; p, p_2) dr_2 dp_2$$

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$$\begin{aligned}
 d(r; p) &= 2 \int d_2(r, r_2; p, p_2) dr_2 dp_2 \\
 &= \sum_{nm} f_{nm}(r, p) d_{nm}
 \end{aligned}$$

$$\text{where } d_{nm} = \int d(r, p) f_{nm}^*(r, p) dr dp.$$

Using the basis of the Laguerre functions we get

$$d_1(r, p) = \sum_n d_{nn}(t) f_{nn}(r, p) \\ + \sum_n d_{n+2,n}(t) f_{n+2,n}(r, p) + d_{n,n+2}(t) f_{n,n+2}(r, p),$$

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where $D = [d_{ij}]$ is a symmetric pentadiagonal matrix:

$$(1-t^2)^2 \begin{pmatrix} 1 & 0 & \alpha_0 t & 0 & 0 & \dots \\ 0 & 1+2t^2 & 0 & \alpha_1 t^3 & 0 & \dots \\ \alpha_0 t & 0 & 2t^2+3t^4 & 0 & \alpha_2 t^5 & \dots \\ 0 & \alpha_1 t^3 & 0 & 3t^4+4t^6 & 0 & \dots \\ 0 & 0 & \alpha_2 t^5 & 0 & 4t^6+5t^8 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

Here $t = \frac{\sqrt{\omega} - \sqrt{\mu}}{\sqrt{\omega} + \sqrt{\mu}}$.

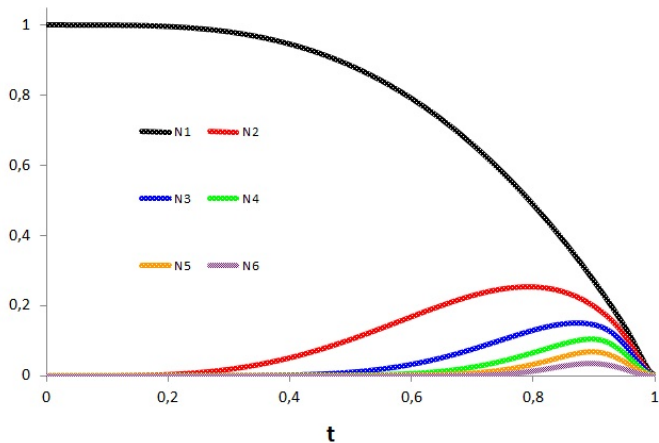


Figure: First six eigenvalues (occupation numbers).

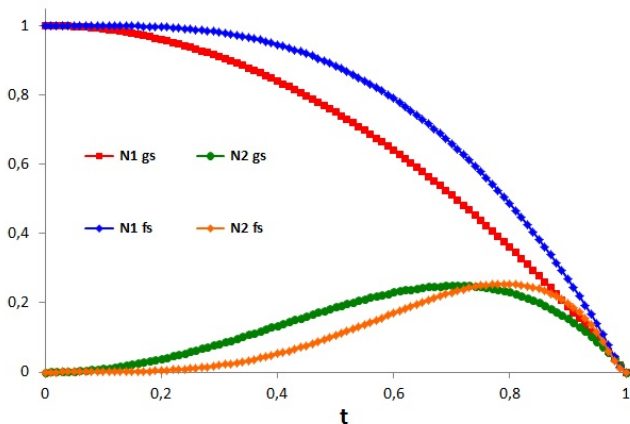


Figure: First (red line) and second (green) occupation numbers of the ground state and the first (blue) and second (orange) occupation numbers of the first excited state.

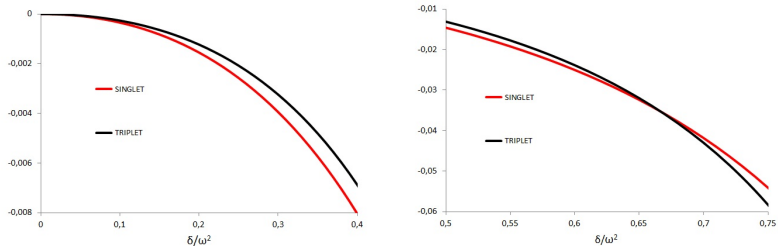


Figure: *Relative correlation energy of the singlet and of the triplet excited mode. As expected, the relative correlation energy for the singlet is greater than for the triplet for small values of the coupling. At $\delta/\omega^2 \sim 0.67$ the order is inverted.*

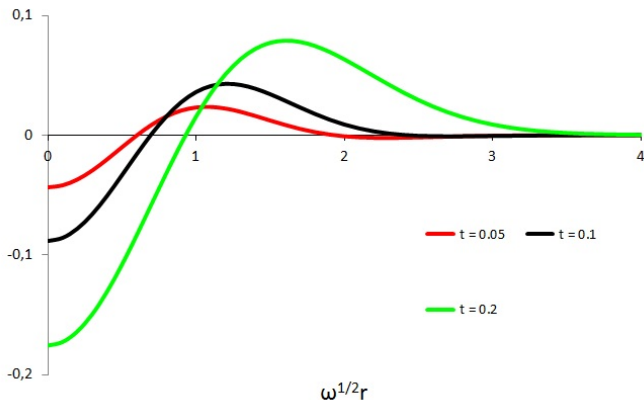


Figure: Moshinsky's hole for the triplet: $(\rho(r) - \rho_{\text{HF}}(r))/\omega^{1/2}$ as a function of $\omega^{1/2}r$.