WIAS

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Kohn-Sham-systems at zero temperature

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1 Introduction: Kohn-Sham systems at zero temperature

Hohenberg-Kohn in [Phys. Review B, 1964] and Kohn-Sham in [Phys. Review A, 1965]

$$\mathcal{E}[u] = -\frac{\hbar^2}{2m}\sum_{n=1}^{N}\int |\nabla\varphi_n(\mathrm{r})|^2 d^3\mathrm{r}$$

$$-\frac{q^2}{4\pi\epsilon_0}\sum_{k=1}^{M}\int \frac{Z_k u(\mathrm{r})}{|\mathrm{r}-\mathrm{R}_k|}d^3\mathrm{r} + \frac{q^2}{2}\int\int \frac{u(\mathrm{r})u(\mathrm{r}')}{4\pi\epsilon_0|\mathrm{r}-\mathrm{r}'|}d^3\mathrm{r}d^3\mathrm{r}' + \int \varepsilon_{xc}[u](\mathrm{r})d^3\mathrm{r},$$

- M is the number of positive ions
- Z_k their atomic number,
- R_k the positions of ions,
- q is the magnitude of the elementary charge,
- ϵ_0 is the vacuum permittivity,
- $\varepsilon_{xc}[u]$ is the so-called exchange correlation energy density

The particle density is given by

$$u(\mathbf{r}) := 2\sum_{n=1}^{N} |\psi_n(\mathbf{r})|^2 \qquad \text{(zero temperature!)},$$

where ψ_n are eigenfunctions satisfying

$$\left(-\frac{\hbar^2}{2m}\Delta - \frac{q^2}{4\pi\epsilon_0}\sum_{k=1}^{M}\frac{Z_k}{|\mathbf{r}-\mathbf{R}_k|} + q^2\int\frac{u(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}' + V_{xc}[u](\mathbf{r})\right)\psi_n = E_n\psi_n.$$

- $V_{xc}[u](\mathbf{r}) := \frac{\partial(\varepsilon_{xc}[u](\mathbf{r}))}{\partial u}$;
- $V_0(\mathbf{r}) := -\frac{q^2}{4\pi\epsilon_0}\sum_{k=1}^{M}\frac{Z_k}{|\mathbf{r}-\mathbf{R}_k|}$;
- $\varphi(\mathbf{r}) := -q\int\frac{u(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}'$ is a the solution of the Poisson equation

$$\Delta\varphi(\mathbf{r}) = \frac{qu(\mathbf{r})}{\epsilon_0}.$$

2 Kohn-Sham systems

Schrödinger operator of the form

$$H_V = -\frac{\hbar^2}{2m}\Delta + V \tag{1}$$

with the effective Kohn-Sham potential

$$V := V_0 + V_{xc}[u] - q\varphi, \tag{2}$$

where the density is given by

$$u(\mathrm{r}) := 2\sum_{n=1}^{N} |\psi_n(\mathrm{r})|^2$$

and φ has to satisfy the Poisson equation

$$\Delta\varphi(\mathrm{r}) = \frac{qu(\mathrm{r})}{\epsilon_0}$$

3 Schrödinger-Poisson-X^α

The model is very flexible and widely applicable because the exchange correlation term can be well adapted to a great variety of problems.

- X^α-exchange correlation potentials:
$$V_{xc}[u] = -C_\alpha |u(x)|^\alpha, \quad \alpha \in (0, 4/3];$$
- Hartree-Fock-Slater approximation:
$$V_{xc}[u] = -C_{1/3} |u(x)|^{1/3},$$
It corresponds to the so-called low-density limit of the Hartree-Fock approximation for N electrons.
- Thomas-Fermi correction:
$$V_{xc}[u] = -C_{2/3} |u(x)|^{2/3}$$
It corresponds to the high-charge-of-nuclei limit.

4 Temperature $T > 0$

Mermin [Phys. Rev. A, 1965]

$$u(\mathrm{r}) := 2\sum_{n=1}^{\infty} \frac{1}{1+e^{\beta(E_n-\mu)}}|\psi_n(\mathrm{r})|^2,$$

where μ is the so called chemical potential and

$$N = \int u(\mathrm{r})d^3\mathrm{r} = 2\sum_{n=1}^{\infty} \frac{1}{1+e^{(E_n-\mu)/kT}},$$

5 Particle density for planar nanostructures

$$\Psi_{\mathbf{k}_\perp,l}(\mathbf{r}) = \frac{e^{i\mathbf{k}_\perp \mathbf{r}_\perp}}{2\pi}\psi_l(x), \quad x \in [x_l, x_r], \quad r_\perp \in \mathbb{R}^2.$$

total energy: $E = \frac{\hbar^2 k_\perp^2}{2m_\perp} + \lambda_l$.

- $\mathbf{r}_\perp = (y, z)$ represents the transversal coordinates;
- $\mathbf{k}_\perp = (k_y, k_z)$ the transversal wave number;
- $m_\perp$ the effective mass in the transversal direction.

$\psi_l(x)$ are the eigenfunctions of the 1D Schrödinger operator

$$H_V := -\frac{\hbar^2}{2}\frac{d}{dx}\left(m^{-1}\frac{d}{dx}\right) + V,$$

where $m = m(x)$ is the position dependent effective mass and V is an effective Kohn-Sham potential.

At zero temperature the density is given by

$$u(\mathbf{r}) = 2 \underbrace{\int d\mathbf{k}_\perp \sum_l}_{E \le E_F} |\Psi_{\mathbf{k}_\perp,l}(\mathbf{r})|^2,$$

which yields

$$u(x) = 2 \sum_{l=1}^{N_F} \frac{|\psi_l(x)|^2}{(2\pi)^2} \int_0^{k_{\perp,F}^{(l)}} 1 \; d\mathbf{k}_\perp,$$

where the sum runs up to the last occupied level $\lambda_{N_F} \le E_F$ and the integral is taken up to a maximum value of the transversal wave number $k_{\perp,F}^{(l)} = \sqrt{\frac{2m_\perp}{\hbar^2}(E_F - \lambda_l)}$;

$$\begin{aligned} u(x) &= 2\frac{m_\perp}{2\pi\hbar^2} \sum_{l=1}^{N_F} |\psi_l(x)|^2 \, (E_F - \lambda_l) \\ &= 2\frac{m_\perp}{2\pi\hbar^2} \sum_{l=1}^{\infty} |\psi_l(x)|^2 \Theta(E_F - \lambda_l) \end{aligned}$$

At temperature $T > 0$ is given by

$$\begin{aligned} u(\mathbf{r}) &= 2 \underbrace{\int d\mathbf{k}_\perp \sum_l}_{0 \le E \le \infty} |\Psi_{\mathbf{k}_\perp, l}(\mathbf{r})|^2 f_{FD}(E, \mu) \\ &= 2 \int_0^\infty d\mathbf{k}_\perp \sum_{l=1}^\infty |\Psi_{\mathbf{k}_\perp, l}(\mathbf{r})|^2 f_{FD}(E, \mu), \end{aligned}$$

where $f_{FD}(E, \mu)$ is the Fermi-Dirac distribution function

$$f_{FD}(E, \mu) = \frac{1}{1 + e^{\frac{E-\mu}{kT}}},$$

k is the Boltzmann constant and μ is the chemical potential. Finally

$$u(x) = 2 \frac{m_\perp}{2\pi \hbar^2} kT \sum_{l=1}^\infty |\psi_l(x)|^2 \ln\left(1 + e^{\frac{\mu - \lambda_l}{kT}}\right),$$

6 Quasi 1D Kohn-Sham systems

- Poisson equation: $-\frac{d}{dx}\left(\varepsilon\frac{d}{dx}\varphi\right) = D - qu$ on $\Omega = [0,1]$;

- boundary conditions: $\varphi(0) = \varphi_0 \in \mathbb{R}$ and $\varphi(1) = \varphi_1 \in \mathbb{R}$;

- Schrödinger operator: $H_V := -\frac{\hbar^2}{2}\frac{d}{dx}\left(m^{-1}\frac{d}{dx}\right) + V$, supplemented by Dirichlet boundary conditions;

- : potential: $V = V_0 + V_{sc}(u) - q\varphi$;

- particle density: $u(V)(x) = 2\sum_{l=1}^{\infty} f(\lambda_l(V) - \mu_f(V))\,|\psi_l(V)(x)|^2, \quad x \in (0,1)$;

- chemical potential: $2\sum_{l=1}^{\infty} f(\lambda_l(V) - \mu_f(V)) = N$.

7 Assumptions

Assumption 7.1. The dielectric permittivity ε is a real, non-negative function obeying $\varepsilon \in L^\infty$ and $\frac{1}{\varepsilon} \in L^\infty$.

Assumption 7.2. The density of ionized dopants D is a 'real distribution' from $W^{-1,2}$.

Assumption 7.3. The effective mass m is a real, non-negative function obeying $m \in L^\infty$ and $\frac{1}{m} \in L^\infty$.

Assumption 7.4.

a) V_0 is a real-valued L^1 function;

b) the exchange–correlation term $V_{xc}(u)$ is a continuous and bounded mapping from L^1 into L^1. This assumption covers the Hartree-Fock-Slater and Thomas-Fermi exchange–correlation terms.

Assumption 7.5. The distribution functions $f : \mathbb{R} \mapsto [0, \infty)$ obey

(i) there is a $t \in]-\infty, \infty[$ such that f is strictly monotonously decreasing on the interval $]-\infty, t[$ and zero on $[t, \infty[$ ($T = 0$)

(ii) the function f obeys $f(s) > 0$ for any $s \in \mathbb{R}$ and

$$\sup_{s \in [1,\infty[} f(s)s^2 < \infty.$$

is valid ($T > 0$).

Particle density operator: $\mathcal{N}_f(\cdot) : L^1 \longrightarrow L^1$,

$$\mathcal{N}_f(V)(x) := 2\sum_l f(\lambda_l(V) - \mu_f(V))\left|\psi_l(V)(x)\right|^2, \quad x \in [0,1]$$

$$\int_0^1 \mathcal{N}_f(V)dx = 2\sum_{l=1}^{\infty} f(\lambda_l(V) - \mu_f(V)) = N.$$

8 Solution

Let $u \in L^1_N$,

$$u \in L^1_N := \left\{ u \in L^1 : u \geq 0, \quad \int_0^1 u dx = N \right\}.$$

The pair $\{\varphi(u), u\}$ is called a solution of the Kohn-Sham system

(i) if $\varphi(u)$ is a solution of the Poisson equation $-\frac{d}{dx}\left(\varepsilon \frac{d}{dx}\varphi\right) = D - qu$, $\Omega = [0, 1]$;

(ii) $u = \mathcal{N}_f(V_0 + V_{xc}(u) - q\varphi(u))$.

Theorem 8.1.

(i) *the pair $\{\varphi(u), u\}$ is a solution of the Kohn-Sham system if and only if $u \in L^1_N$ is a fixed point of Φ_f,*

$$\Phi_f(u) := \mathcal{N}_f(V_0 + V_{xc}(u) - q\varphi(u)) : L^1_N \mapsto L^1_N; \tag{3}$$

(ii) *the mapping Φ_f has a fixed point.*

9 Monotonicity

A map $A(\cdot) : \mathfrak{X}_{\mathbb{R}} \mapsto \mathfrak{X}^*_{\mathbb{R}}$ is called monotone if

$$< A(u) - A(v), u - v > \geq 0, \qquad U, V \in \mathfrak{X}_{\mathbb{R}}.$$

Theorem 9.1. *Let H be a self-adjoint operator in the separable Hilbert space $\mathcal{H}$ with compact resolvent and let U and V be bounded, self-adjoint operators on $\mathcal{H}$. If $f : \mathbb{R} \longrightarrow \mathbb{R}$ is a Borel measurable function such that $f(H+U)$ and $f(H+V)$ are trace class operators, then the formula*

$$\operatorname{tr}([f(H+U) - f(H+V)](U-V)) = \sum_{k,l=1}^{\infty} (f(\lambda_k) - f(\mu_l))(\lambda_k - \mu_l)|\langle \psi_k, \xi_l \rangle|^2$$

is valid. Here $\{\lambda_k\}_k$ ($\{\mu_l\}_l$) is the sequence of eigenvalues of $H+U$ ($H+V$) and $\{\psi_k\}_k$ ($\{\xi_l\}_l$) is an – orthornormalized – sequence of corresponding eigenvectors.

Example: $\mathfrak{B}(\mathcal{H}) \ni U \mapsto f(U) \in \mathfrak{B}_1(\mathcal{H}) \subseteq \mathfrak{B}(\mathcal{H})^*$ is monotone if $f(\cdot) : \mathbb{R} \longrightarrow \mathbb{R}$ is monotone.

Corollary 9.2. *The mappings* $L^1_{\mathbb{R}} \ni V \longrightarrow -\mathcal{N}_f(V) \in L^\infty_{\mathbb{R}}$ *and* $W^{1,2}_{0,\mathbb{R}} \ni V \longrightarrow -\mathcal{N}_f(V) \in W^{-1,2}_{\mathbb{R}}$ *are monotone.*

A map $A(\cdot) : \mathfrak{X}_{\mathbb{R}} \mapsto \mathfrak{X}^*_{\mathbb{R}}$ is called strongly monotone if

$$< A(u) - A(v), u - v > \geq c\|u - v\|^2,$$

for $u, v \in \mathfrak{X}_{\mathbb{R}}$.

Theorem 9.3. *If* $A(\cdot) : \mathfrak{X}_{\mathbb{R}} \mapsto \mathfrak{X}^*_{\mathbb{R}}$ *is continuous and strongly monotone, then there exists the inverse operator* $A^{-1} : \mathfrak{X}^*_{\mathbb{R}} \mapsto \mathfrak{X}_{\mathbb{R}}$ *and is even Lipschitz continuous. If* A *is in addition Lipschitz continuous, then* A^{-1} *is also strongly monotone.*

Theorem 9.4. *If the correlation term V_{xc} is absent, then the Kohn-Sham system has a unique solution* $\{\varphi, u\}$.

Proof idea: We have

$$-\frac{d}{dx}\varepsilon\frac{d}{dx}\varphi + q\mathcal{N}_f(V_0 - q\varphi) = D, \quad \varphi(0) = \varphi_0, \quad \varphi(1) = \varphi_1$$

We find a solution $\widehat{\varphi} \in W^{1,2}_{\mathbb{R}}$ obeying

$$-\frac{d}{dx}\varepsilon\frac{d}{dx}\widehat{\varphi} = 0, \quad \widehat{\varphi}(0) = \varphi_0, \quad \widehat{\varphi}(1) = \varphi_1$$

and set $\varphi = \widehat{\varphi} + \phi$, $\phi \in W^{1,2}_{0,\mathbb{R}}$, that is, $\phi(0) = \phi(1) = 0$.

$$\underbrace{-\frac{d}{dx}\varepsilon\frac{d}{dx}\phi + q\mathcal{N}_f(\overbrace{V_0 - q\widehat{\varphi}}^{\widehat{V}_0} - \phi)}_{\text{strongly monotone operator from } W^{1,2}_{0,\mathbb{R}} \mapsto W^{-1,2}_{0,\mathbb{R}}} = D$$

Hence the Poisson equation possesses a unique solution.

10 Convergence

Let

$$f_{FD}(E,\mu,T) = \frac{1}{1+e^{(E-\mu)/kT}}, \qquad T > 0,$$

and

$$f_{FD}(E,\mu,0) = \Theta(\mu - E), \qquad T = 0.$$

Hence every solution of the Kohn-Sham systems depends on $T \geq 0$.

Problem: Let $\{\varphi(u_T), u_T\}$ be a solution of the Kohn-Sham system for a given temperature $T \geq 0$. Does the limit

$$\lim_{T\to 0}\{\varphi(u_T), u_T)\} =?$$

exists in the topology of $L^\infty \times L^1$ and is it true that $\{\varphi(u_0), u_0\}$

$$\lim_{T\to 0}\{\varphi(u_T), u_T)\} = \{\varphi(u_0), u_0\}?$$

is a solution of the Kohn-Sham-system at $T = 0$.

Theorem 10.1.

(i) The limit $\lim_{T\to 0}\{\varphi(u_T), u_T)\} = \{\varphi(u_0), u_0\}$ *exists in the* $L^\infty \times L^1$ *topology and is a solution of the Kohn-Sham-system at* $T = 0$.

(ii) If the V_{xc} *is absent, then the unique solutions* $\lim_{T\to 0}\{\varphi(u_T), u_T\}$ *converge to the unique solution at* $T = 0$.