

Dissociation limit in Kohn-Sham density functional theory

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Abstract

We consider the dissociation limit for molecules of the type X_2 in the Kohn-Sham density functional theory setting, where X can be any element. We prove that when the two atoms in the system are torn infinitely far apart, the energy of the system converges to $\min_{\alpha \in [0, N]} (I_\alpha^X + I_{2N-\alpha}^X)$, where I_α^X denotes the energy of the atom with α electrons surrounding it. Depending on the “strength” of the exchange this minimum might not be equal to the symmetric splitting $2I_N^X$. We show numerically that for the H_2 -molecule with Dirac exchange this gives the expected result of twice the energy of a H-atom $2I_1^H$.

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1 Introduction

Density functional theory (DFT) was developed by Hohenberg, Kohn and Sham [15, 17] in the 1960s and is to this day one of the most widely spread electronic structure models in quantum chemistry, biology and materials science because of its good compromise between accuracy and computational cost. The idea behind DFT is to transform the high-dimensional Schrödinger equation into a low-dimensional and thus computationally manageable problem.

The trade-off in this approach is the introduction of the so-called exchange-correlation functional, which is in theory exact but in practice unknown. Therefore a lot of effort [32, 31, 3, 33, 29] has gone into building good approximations to this functional. In this paper we consider the simplest form of these models, the local density approximation (LDA). Even here the resulting mathematical properties are still far from being understood. Furthermore as observed in [27] starting in the early 2000s newer approximations actually become worse in predicting the electron densities. This is due to only focusing on the energies and in the process sacrificing mathematical rigor in favor of the flexibility of fitting to empirical data. Thus in the present article we want to focus on fundamental properties that the exchange-correlation functional should fulfill.

Our main goal is to analyze the dissociation limit of any symmetric diatomic molecule, i.e. any molecule of the form X_2 , in Kohn-Sham (KS) DFT. Simply put we ask the question, what happens to the energy of the system, when the distance between the two atoms is artificially increased further and further until they are torn infinitely far apart? Our main result takes the following form

Theorem (Theorem 1 – Informal Version). *Let $I_{2N,R}^{X_2}$ and I_λ^X be the energy of the X_2 -molecule with distance R between the atoms and the X -atom with λ electrons defined by (20). Then we have*

$$\lim_{R \rightarrow \infty} I_{2N,R}^{X_2} = \min_{\alpha \in [0, N]} (I_\alpha^X + I_{2N-\alpha}^X). \quad (1)$$

In the long range limit, the ground-state energy of the X_2 -molecule is identical to the energy of two non-interacting atoms - one with electron mass α and one with electron mass $2N - \alpha$. The physical expectation here is, that it is optimal to split the electrons evenly (i.e. the minimum is attained for $\alpha = N$).

The question if or rather for which λ one has symmetric splitting, i.e.

$$2I_\lambda < I_{\lambda+\varepsilon} + I_{\lambda-\varepsilon} \quad \text{for all } 0 < \varepsilon < \lambda,$$

already plays an important role in Thomas-Fermi and related theories, see e.g. [21].

To our knowledge the fact that the lowest energy splitting is always given by two neutral atoms is not even proven in full quantum mechanics, rather only in Thomas-Fermi theory and perturbations thereof, where the behaviour of the energy with respect to the particle number is completely understood. A simple sketch of this is presented in Figure 1.

Note furthermore that in full quantum mechanics and thus for exact HK-DFT charge quantization occurs, i.e. α in (1) can be restricted to integer values, as proven in [10].

As will be discussed in detail in Section 3 if the exchange becomes too strong, we observe symmetry breaking, i.e. the right hand side of (1) does not equal $2I_N^X$.

In the physics literature, this is a well-known challenge: While spin-restricted Kohn-Sham calculations yield qualitatively correct results (i.e. by nature preserve spin-symmetry) they only give reasonable energies close to the actual bond length. Spin unrestricted schemes on the other hand yield better energies but may prefer ionic solutions at long ranges [11, 30].

This dilemma has recently attracted mathematical interest. In case of the H_2 molecule at fixed bond-length (see [16]) and for periodic systems (see [14]), symmetry breaking occurs for

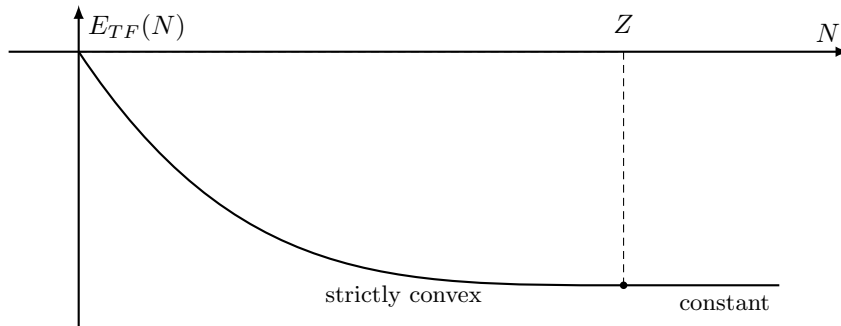


Figure 1: The Thomas-Fermi energy $E_{TF}(N)$ with respect to the particle number N . For positively charged systems $N < Z$ it is strictly convex, for $N > Z$ it remains constant.

sufficiently strong exchange contributions. These issues in LDA-DFT and related theories like Thomas-Fermi-Dirac-von Weizsäcker is caused by the Dirac term $-\int \rho^{4/3}$, which to some extent makes the functional concave and can thus lead also to nonattainment, see e.g. [25].

The rest of the paper is structured as follows: The next section sets the stage by defining and motivating all the energy functionals needed, giving our main result in Theorem 1 the necessary detail. In Section 3 we put it into context by considering first a one-dimensional DFT model where we can always determine the right hand side of (1). Then we consider the full three dimensional case and fill the gap in our theoretical results by numerical evidence.

The last section contains all the proofs, with the most interesting point being that we apply the concentration-compactness lemma not to a minimizing sequence but to a sequence of minimizers. Figure 4 summarizes the structure of the proof to help not get lost in technical details.

2 Setting the stage

2.1 Density functional theory

To put our result into perspective we recall here shortly the basic fundamentals of DFT. A standard reference would be [28]. Readers familiar with the topic might want to skip this section.

The starting point is a system of N non-relativistic electrons under influence of an external potential $v(x)$ and with a repulsive interaction potential $v_{ee}(x-y)$ (Born-Oppenheimer approximation).

For a molecule with M atomic nuclei at positions $R_1, \dots, R_M \in \mathbb{R}^3$, with individual charges $Z_1, \dots, Z_M \in \mathbb{N}$ and total atomic charge $Z = \sum_{i=1}^M Z_i$, and with N electrons the potential $v(x)$ is

just the ensuing Coulomb potential of their positions and charges

$$v(x) := - \sum_{i=1}^M \frac{Z_i}{|x - R_i|}, \quad x \in \mathbb{R}^3.$$

The class of admissible functions \mathcal{A} – the so-called N -electron wave functions – is given by

$$\mathcal{A} := \{ \Psi \in L^2((\mathbb{R}^3 \times \Sigma)^N; \mathbb{C}) : \nabla \Psi \in L^2, \Psi \text{ antisymmetric, } \|\Psi\|_{L^2} = 1 \},$$

where $\Sigma := \{|\uparrow\rangle, |\downarrow\rangle\}$ denotes the set of spin-states.

Now we can finally define the energy functional \mathcal{E}^{QM} ,

$$\mathcal{E}^{QM}[\Psi] := T[\Psi] + V_{ne}[\Psi] + V_{ee}[\Psi], \quad (2)$$

where

$$T[\Psi] := \frac{1}{2} \int_{(\mathbb{R}^3_\Sigma)^N} \sum_{i=1}^N |\nabla_{x_i} \Psi(x_1, s_1, \dots, x_N, s_N)|^2 dz_1 \dots dz_N$$

describes the kinetic energy,

$$V_{ne}[\Psi] := \int_{(\mathbb{R}^3_\Sigma)^N} \sum_{i=1}^N v(x_i) |\Psi(x_1, s_1, \dots, x_N, s_N)|^2 dz_1 \dots dz_N$$

gives the electron-nuclei interaction energy, and

$$V_{ee}[\Psi] := \int_{(\mathbb{R}^3_\Sigma)^N} \sum_{1 \leq i < j \leq N} v_{ee}(x_i - x_j) |\Psi(x_1, s_1, \dots, x_N, s_N)|^2 dz_1 \dots dz_N$$

is the electron-electron interaction energy. The exact quantum mechanical ground state energy is now defined as

$$E_0^{QM} := \inf_{\Psi \in \mathcal{A}} \mathcal{E}^{QM}[\Psi]. \quad (3)$$

Unfortunately due to the curse of dimensionality there is no hope of ever solving (3) for interesting molecular systems. Hence in Kohn-Sham (KS) DFT one does not consider the wave function Ψ but the one-body electron-density

$$\rho(x) = \int_{\mathbb{R}^{3(N-1)}} |\Psi(x, z_2, \dots, z_N)|^2 dz_2 \dots dz_N.$$

This leads to a nonlinear PDE system for the density. The energy is then given by the KS energy functional

$$\mathcal{E}[\Phi] = \sum_{\alpha} \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \varphi_{\alpha}|^2 + \int_{\mathbb{R}^3} v \rho dx + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx dy + E_{xc}[\rho],$$

where Φ denotes the collection of the orbitals $(\varphi_{\alpha})_{\alpha}$ and $\rho = \sum_{\alpha} |\varphi_{\alpha}|^2$.

The Hohenberg-Kohn theorem [15] guarantees the existence of a functional $E_{xc}[\rho]$ – depending only on the density – such that KS energy gives the same as exact N -body Schrödinger equation. Meaning if we knew the exact functional E_{xc} , we would not lose any information. Hence a lot of effort has been put into creating applicable approximations to this functional [31, 32, 3, 29].

The prototypical example for an $E_{xc}[\rho]$ -approximation is given by

$$E_{xc}[\rho] = \int_{\mathbb{R}^3} e_{xc}(\rho(x)) dx, \quad e_{xc} = -c_{xc} \rho^{4/3}. \quad (4)$$

2.2 Mixed-states

This section shortly recalls the description using mixed states, i.e. density matrices. Let \mathfrak{S}_1 denote the vector space of trace class operators on $L^2(\mathbb{R}^3)$ and introduce the subspace $\mathcal{H} := \{\gamma \in \mathfrak{S}_1 : |\nabla|\gamma|\nabla| \in \mathfrak{S}_1\}$ endowed with the norm $\|\cdot\|_{\mathcal{H}} := \text{tr}(|\cdot|) + \text{tr}(|\nabla|\cdot|\nabla|)$ and the convex set $K := \{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) : 0 \leq \gamma \leq 1, \text{tr}(\gamma) < \infty, \text{tr}(|\nabla|\gamma|\nabla|) < \infty\}$. Let us first remark that

$$E_0^{QM} = \inf \left\{ \langle \Psi | H_N^V | \Psi \rangle : \Psi \in \mathcal{A} \right\} \quad (5)$$

$$= \inf \left\{ \text{tr}(H_N^V \Gamma) : \Gamma \in D_N \right\}, \quad (6)$$

where D_N is the set of N -body density matrices defined by

$$D_N = \left\{ \Gamma \in \mathcal{S}(\mathcal{H}_N) : 0 \leq \Gamma \leq 1, \text{tr}(\Gamma) = 1, \text{tr}(-\Delta\Gamma) < \infty \right\}. \quad (7)$$

In the above expression, $\mathcal{S}(\mathcal{H}_N)$ denotes the vector space of bounded self-adjoint operators on \mathcal{H}_N and the condition $0 \leq \Gamma \leq 1$ stands for $0 \leq \langle \Psi | \Gamma | \Psi \rangle \leq \|\Psi\|_{\mathcal{H}_N}^2$ for all $\Psi \in \mathcal{H}_N$.

From a physical point of view, (5) and (6) mean that the ground state energy can be computed either by minimizing over pure states – characterized by wave functions Ψ – or by minimizing over mixed states – characterized by density operators Γ .

As before we define the electronic density for any N -electron density operator $\Gamma \in D_N$

$$\rho_\Gamma(x) := N \sum_{\sigma \in \Sigma} \int_{(\mathbb{R}_\Sigma^3)^{(N-1)}} \Gamma(x, \sigma, z_2, \dots, z_N; x, \sigma, z_2, \dots, z_N) dz_2 \dots dz_N. \quad (8)$$

Note that here and below we use the same notation for an operator and its Green kernel.

Then we get for the electron densities

$$\left\{ \rho : \mathbb{R}^3 \rightarrow \mathbb{R} : \exists \Gamma \in D_N, \rho_\Gamma = \rho \right\} = \mathcal{R} = \left\{ \rho : \mathbb{R}^3 \rightarrow \mathbb{R} : \rho \geq 0, \sqrt{\rho} \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho dx = N \right\}.$$

Let Γ be in the above admissible set, the one-electron reduced density operator Υ_Γ associated with Γ which is the self-adjoint operator on $L^2(\mathbb{R}_\Sigma^3)$ with kernel

$$\Upsilon_\Gamma(x, y) = N \int_{(\mathbb{R}_\Sigma^3)^{N-1}} \Gamma(x, z_2, \dots, z_N; y, z_2, \dots, z_N) dz_2 \dots dz_N.$$

Furthermore it is known, see e.g. [7], that

$$\left\{ \Upsilon : \exists \Gamma \in D_N, \rho_\Gamma = \rho \right\} = \left\{ \Upsilon \in \mathcal{R}D_N : \rho_\Upsilon = \rho \right\}, \quad (9)$$

where

$$\mathcal{R}D_N = \left\{ \Upsilon \in L^2(\mathbb{R}_\Sigma^3) : 0 \leq \Upsilon \leq 1, \text{tr}(\Upsilon) = N, \text{tr}(-\Delta_x \Upsilon) < \infty \right\} \quad \text{and} \quad (10)$$

$$\rho_\Upsilon(x) := \sum_{\sigma \in \Sigma} \Upsilon(x, \sigma; x, \sigma). \quad (11)$$

This leads to the so-called extended Kohn-Sham models

$$I_N^{EKS}[V] := \inf \left\{ \text{tr} \left(-\frac{1}{2} \Delta_x \Upsilon \right) + \int_{\mathbb{R}^3} \rho_\Upsilon V \, dx + J[\rho_\Upsilon] + E_{ex}[\rho_\Upsilon] : \Upsilon \in \mathcal{RD}_N \right\}. \quad (12)$$

Note, up to now no approximation has been made, such that for the exact exchange-correlation functional $E_0^{QM} = I_N^{EKS}$ for any molecular system containing N electrons. Unfortunately, there is no tractable expression of $E_{xc}[\rho]$ that can be used in numerical simulations.

Before proceeding further, and for the sake of simplicity, we will restrict ourselves to closed-shell, spin-unpolarized systems. This means that we will only consider molecular systems with an even number of electrons $N = 2N_p$, where N_p is the number of electron pairs in the system, and we will assume that electrons “go by pairs”.

Hence, the constraints on the one-electron reduced density operator originating from the closed-shell approximation read:

$$\Upsilon(x, |\uparrow\rangle, y, |\uparrow\rangle) = \Upsilon(x, |\downarrow\rangle, y, |\downarrow\rangle) \quad \text{and} \quad \Upsilon(x, |\uparrow\rangle, y, |\downarrow\rangle) = \Upsilon(x, |\downarrow\rangle, y, |\uparrow\rangle) = 0. \quad (13)$$

Introducing $\gamma(x, y) = \Upsilon(x, |\uparrow\rangle, y, |\uparrow\rangle)$ and denoting $\rho_\gamma(x) = 2\gamma(x, x)$, we obtain the spin-unpolarized extended Kohn-Sham model

$$I_N^{REKS}(V) = \inf \left\{ \mathcal{E}(\gamma) : \gamma \in K_{N_p} \right\}, \quad (14)$$

where the energy functional \mathcal{E} is given by

$$\mathcal{E}(\gamma) = \text{tr}(-\Delta\gamma) + \int_{\mathbb{R}^3} \rho_\gamma V \, dx + J[\rho_\gamma] + E_{xc}[\rho_\gamma], \quad (15)$$

and the admissible set looks like

$$K_{N_p} = \left\{ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) : 0 \leq \gamma \leq 1, \text{tr}(\gamma) = N_p, \text{tr}(-\Delta\gamma) < \infty \right\}. \quad (16)$$

Note that the factor $\frac{1}{2}$ in front of the trace vanishes due to the definition of γ and accounts for the spin.

Furthermore, by spectral theory we have for any $\gamma \in K_{N_p}$

$$\gamma = \sum_{i \geq 1} \lambda_i |\varphi_i\rangle \langle \varphi_i| \quad (17)$$

with

$$\varphi_i \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} \varphi_i \varphi_j \, dx = \delta_{ij}, \quad \lambda_i \in [0, 1], \quad \sum_{i=1}^{\infty} \lambda_i = N_p, \quad \sum_{i=1}^{\infty} \lambda_i \|\nabla \varphi_i\|_{L^2}^2 < \infty. \quad (18)$$

2.3 Dissociation

In this section we shortly introduce the energy functionals we will be using in this paper. The Kohn-Sham energy functional is given by

$$\mathcal{E}^V[\gamma] := \text{tr}[-\Delta\gamma] + \int_{\mathbb{R}^3} V\rho \, dx + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} \, dx \, dy + \int_{\mathbb{R}^3} e_{xc}(\rho(x)) \, dx, \quad (19)$$

where $\rho(x) = 2\gamma(x, x)$ and V denotes the external potential. Note that the factor 2 is used since we are considering a spin-unpolarized system. Let X be any atom with Z number of protons. Then for the X_2 molecule we have

$$V_R^{X_2} = -\frac{Z}{|\cdot|} - \frac{Z}{|\cdot - R|}, \quad \mathcal{E}_R^{X_2}[\gamma] := \mathcal{E}^{V_R^{X_2}}[\gamma],$$

and similar for the X -atom

$$V^X = -\frac{Z}{|\cdot|}, \quad \mathcal{E}^X[\gamma] := \mathcal{E}^{V^X}[\gamma].$$

Here and in the following to keep notation a bit simpler we will denote by R the position of the second nucleus and also its distance to the origin, as long as it is clear from context which one we are referring to.

We then define the ground state energies

$$I_{\lambda, R}^{X_2} := \inf_{\gamma \in K_\lambda} \mathcal{E}_R^{X_2}[\gamma], \quad I_\lambda^X := \inf_{\gamma \in K_\lambda} \mathcal{E}^X[\gamma], \quad (20)$$

where the admissible set is given by

$$K_\lambda := \{\gamma \in S(L^2(\mathbb{R}^3)) : 0 \leq \gamma \leq 1, \text{tr}(\gamma) = \lambda, \text{tr}(-\Delta \gamma) < \infty\}. \quad (21)$$

Furthermore we introduce the problem at infinity, corresponding to a system without nuclei

$$I_\lambda^\infty := \inf_{\gamma \in K_\lambda} \mathcal{E}^\infty[\gamma], \quad \mathcal{E}^\infty[\gamma] := \text{tr}[-\Delta \gamma] + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx dy + \int_{\mathbb{R}^3} e_{xc}(\rho) dx. \quad (22)$$

To shorten notation we will denote by $T[\gamma] = \text{tr}[-\Delta \gamma]$ the kinetic energy, $V[\gamma] = \int V(x)\rho(x)$ describes the electron-nuclei interaction, $J[\rho] = \frac{1}{2} \int \int \frac{\rho(x)\rho(y)}{|x-y|}$ is the Hartree energy and the exchange-correlation term is given by $E_{xc}[\rho] = \int e_{xc}(\rho)$. In addition define the bilinear form corresponding to J by $D[f, g] = \int \int \frac{f(x)g(y)}{|x-y|}$. Furthermore if the statement holds true for all of the three infima, we simply write I_λ .

Next let us give the assumption on the exchange-correlation term. Note that we can use the same setting as [1] for the local-density approximation (LDA).

Assumption 1 (LDA-exchange-correlation). *Let $e_{xc} : \mathbb{R}_+ \rightarrow \mathbb{R}$ be a C^1 -function such that*

1. $e_{xc}(0) = 0$,
2. $e'_{xc} \leq 0$,
3. $\exists 0 < \beta_- \leq \beta_+ < \frac{2}{3}$ such that $|e'_{xc}(\rho)| \leq C(\rho^{\beta_-} + \rho^{\beta_+})$,
4. $\exists 1 \leq \alpha < \frac{3}{2}$ such that $\limsup_{\rho \rightarrow 0} \frac{e_{xc}(\rho)}{\rho^\alpha} < 0$.

Note that the prototypical exchange-correlation functional in the LDA-setting (4) coming from the uniform electron gas satisfies these assumptions with $\alpha = \frac{4}{3}$ and $\beta_- = \beta_+ = \frac{1}{3}$.

Remark. *The existence of minimizers to these functionals for neutral or positively charged systems is due to [1]. We will also be using the following standard results proven there.*

First some properties of the electron mass to ground state energy map $\lambda \mapsto I_\lambda$.

Lemma 1 (Properties of the infimum [1]). *Let $I_\lambda^{X_2}, I_\lambda^X$ and I_λ^∞ be as defined above. Then the following holds*

1. *All the maps $\lambda \mapsto I_\lambda$ are continuous and strictly decreasing for any $\lambda \geq 0$.*
2. *We always have $I_0 = 0$ and $-\infty < I_{R,\lambda}^{X_2} < I_\lambda^X < I_\lambda^\infty < 0$.*
3. *Furthermore all the I_λ satisfies the subadditivity condition, i.e.*

$$I_\lambda \leq I_\alpha + I_{\lambda-\alpha}^\infty \quad \forall \alpha \in [0, \lambda] \quad (23)$$

Furthermore minimizing sequences for I_λ cannot vanish.

Lemma 2. *The three functionals $\mathcal{E}^{X_2}, \mathcal{E}^X, \mathcal{E}^\infty$ are all continuous on \mathcal{H} .*

The next lemma summarizes the standard bounds on the energy functional. We note that in the following C will describe a generic constant, which may have different values at each appearance, indicating some finite positive constant independent of the surrounding variables.

Lemma 3 (Bounds on the energy functional). *For all $\gamma \in K$, we get $\sqrt{\rho_\gamma} \in H^1(\mathbb{R}^3)$ and the following inequalities:*

(i) *Lower bound on the kinetic energy:*

$$\frac{1}{2} \|\nabla \sqrt{\rho_\gamma}\|_{L^2}^2 \leq \text{tr}[-\Delta \gamma] \quad (24)$$

(ii) *Upper bound on the Coulomb energy:*

$$0 \leq J[\rho_\gamma] \leq C \text{tr}[\gamma]^{\frac{3}{2}} \text{tr}[-\Delta \gamma]^{\frac{1}{2}} \quad (25)$$

(iii) *Bounds on the interaction energy between nuclei and electrons:*

$$-4Z \text{tr}[\gamma]^{\frac{1}{2}} \text{tr}[-\Delta \gamma]^{\frac{1}{2}} \leq \int_{\mathbb{R}^3} \rho_\gamma(x) V(x) dx \leq 0 \quad (26)$$

(iv) *Bounds on the exchange-correlation energy:*

$$-C \left(\text{tr}[\gamma]^{1-\frac{\beta_-}{2}} \text{tr}[-\Delta \gamma]^{\frac{3\beta_-}{2}} + \text{tr}[\gamma]^{1-\frac{\beta_+}{2}} \text{tr}[-\Delta \gamma]^{\frac{3\beta_+}{2}} \right) \leq E_{xc}[\rho_\gamma] \leq 0 \quad (27)$$

(v) Lower bound on the energy:

$$\mathcal{E}[\gamma] \geq \frac{1}{2} \left(\text{tr}[-\Delta \gamma]^{\frac{1}{2}} - 4Z \text{tr}[\gamma]^{\frac{1}{2}} \right)^2 - 8Z^2 \text{tr}[\gamma] - C \left(\text{tr}[\gamma]^{\frac{2-\beta_-}{2-3\beta_-}} + \text{tr}[\gamma]^{\frac{2-\beta_+}{2-3\beta_+}} \right) \quad (28)$$

(vi) Lower bound on the energy at infinity:

$$\mathcal{E}^\infty[\gamma] \geq \frac{1}{2} \text{tr}[-\Delta \gamma] - C \left(\text{tr}[\gamma]^{\frac{2-\beta_-}{2-3\beta_-}} + \text{tr}[\gamma]^{\frac{2-\beta_+}{2-3\beta_+}} \right). \quad (29)$$

In particular, minimizing sequences of I_λ (20) and I_λ^∞ (22) are bounded in \mathcal{H} .

Lemma 3 is a central point for the existence of minimizer in the fixed nuclei setting but more importantly for us it bounds the minimizers independently of the position of the nuclei.

Let us now restate the main result of this paper.

Theorem 1 (Dissociation limit). *Let $I_{\lambda,R}^{X_2}$ and I_λ^X be defined by (20), then we have for positively and neutrally charged molecules, i.e. for $\lambda \leq 2Z$,*

$$\lim_{R \rightarrow \infty} I_{\lambda,R}^{X_2} = \min_{\alpha \in [0,\lambda]} (I_\alpha^X + I_{\lambda-\alpha}^X). \quad (30)$$

Theorem 1 says the energy of the X_2 -molecule converges – as the nuclei are pulled infinitely far apart – to the minimum over distributing the amounts of electrons λ on two separated X -atoms. For linear problems this directly gives $2I_{\lambda/2}^X$, i.e. a symmetric splitting, but for nonlinear problems $\alpha \mapsto I_\alpha^X + I_{\lambda-\alpha}^X$ might take its minimum at another value. Whether the right hand side gives the expected symmetric minimum or not, will be discussed on the basis of the H_2 molecule in the next Section.

We want to stress again that we consider the spin-restricted setting also for the two atoms. Hence applying it to an H-Atom with a single electron has to be taken with a grain of salt.

3 Symmetric Dissociation or not ?

The question which arises now is of course is: Does

$$\min_{\alpha \in [0,1]} (I_\alpha^H + I_{2-\alpha}^H) \stackrel{?}{=} 2I_1^H, \quad (31)$$

hold or not, i.e. do we have the right dissociation limit which we expect from physical intuition or which holds also for the Schrödinger equation. The answer is it depends on the “strength” of the exchange-correlation functional. To discuss this further take $e_{xc}(\rho) = -c_{xc}\rho^{4/3}$ – the prototypical example arising from the homogeneous electron gas – with the constant c_{xc} determining the strength of the exchange term.

To get a better feeling for what determines if the splitting is symmetric or not, i.e. if $\alpha = 1$ is the minimizer in (31), we consider first a one-dimensional model.

3.1 Onedimensional model

As we will see in the following section, it is quite hard to determine when

$$\min_{\alpha} (I_{\alpha}^H + I_{2-\alpha}^H) = 2I_1^H.$$

To understand the problem better we study in this section the one-dimensional problem. Since the Coulomb potential is not well suited for the one dimensional case, we consider $v(x) = \delta_0(x)$, i.e. a simple contact potential [26]. The corresponding full Schrödinger system for the H_2 -molecule looks like

$$E_R^{H_2} = \inf_{\substack{\psi \in H^1(\mathbb{R}^2), \\ \|\psi\|_{L^2} = 1}} \langle \psi, H(x, y)\psi \rangle, \quad H(x, y) = \sum_{z \in \{x, y\}} -\frac{1}{2} \frac{d^2}{dz^2} - \delta_0(z) - \delta_R(z) + \delta_{|x-y|}(z) \quad (32)$$

and the energy for the H -atom becomes

$$E^H = \inf_{\substack{\varphi \in H^1(\mathbb{R}), \\ \|\varphi\|_{L^2} = 1}} \langle \varphi, h(x)\varphi \rangle, \quad h(x) = -\frac{1}{2} \frac{d^2}{dx^2} - \delta_0(x). \quad (33)$$

As for the standard Schrödinger system also here we have the right dissociation limit.

Proposition 1 (Dissociation limit for the Schrödinger setting). *For the full Schrödinger setting we always have*

$$\lim_{R \rightarrow \infty} E_R^{H_2} = 2E^H, \quad (34)$$

i.e. the right dissociation limit.

Proof. See Section 4.3. □

Note that Theorem 1 gives exactly the same result in the nonlinear case, but in the linear case every pair $(\alpha, 2 - \alpha)$ gives the same result, so we always have symmetric dissociation.

Now we consider the DFT version of this system. Note that in this case the Hartree term takes the form

$$J[\rho] = \frac{1}{2} \int \int \rho(x)v(x-y)\rho(y) dx dy = \frac{1}{2} \int \rho^2(x) dx.$$

Furthermore the exchange energy per volume looks like $e_{xc}(\rho) = -c_{xc}\rho^2$, where the exponent is $2 = 1 + \frac{1}{d}$ and $c_{xc} = \frac{1}{4}$ see [26, 18].

In total our energy functional for the H -atom takes the form

$$\begin{aligned} \mathcal{E}^H[\rho] &= \frac{1}{2} \int (\sqrt{\rho'})^2 dx - \int v\rho dx + \frac{1}{2} \int \int \rho(x)\rho(y)v(|x-y|) dx dy + E_{xc}[\rho] \\ &= \frac{1}{2} \int (\sqrt{\rho'})^2 dx - \rho(0) + \left(\frac{1}{2} - c_{xc}\right) \int \rho^2 dx. \end{aligned}$$

And analogously for the H_2 -molecule

$$\mathcal{E}^{H_2}[\rho] = \int (\sqrt{\rho'})^2 dx - \rho(0) - \rho(R) + \left(\frac{1}{2} - c_{xc}\right) \int |\rho|^2 dx.$$

In the same way as in Section 4 we can show the dissociation limit

$$\lim_{R \rightarrow \infty} I_R^{H_2} = \min_{\alpha \in [0,2]} I_\alpha^H + I_{2-\alpha}^H.$$

Due to replacing the Coulomb potential by a contact potential we simplify the problem because the Hartree and the exchange energy take the same form. Hence the energy functional $\rho \mapsto \mathcal{E}^H[\rho]$ is clearly convex for $c_{xc} \leq \frac{1}{2}$.

This property is inherited by the infimum. Take any ρ_α, ρ_β nonnegative and with L^1 -norm α, β , respectively. Then,

$$I_{\lambda\alpha+(1-\lambda)\beta} \leq \mathcal{E}[\lambda\rho_\alpha + (1-\lambda)\rho_\beta] \leq \lambda\mathcal{E}[\rho_\alpha] + (1-\lambda)\mathcal{E}[\rho_\beta],$$

taking the infimum over ρ_α, ρ_β gives the convexity of $\alpha \mapsto I_\alpha$.

Therefore we have for $c_{xc} \leq \frac{1}{2}$

$$2I_1 = 2I_{\frac{1}{2}\alpha + \frac{1}{2}(2-\alpha)} \leq I_\alpha + I_{2-\alpha},$$

so symmetric splitting occurs.

For $c_{xc} > \frac{1}{2}$ there is no symmetric splitting anymore. In order to see this, note that taking the test-functions $(1 \pm \eta)\rho_1$ with ρ_1 the minimizer to I_1 yields

$$I_{1+\eta} + I_{1-\eta} \leq 2I_1 + 2\eta^2\left(\frac{1}{2} - c_{xc}\right) \int \rho_1^2 dx < 2I_1,$$

i.e. $2I_1$ is the strict global maximum. Furthermore in this setting the ground state density can be found explicitly, see e.g. [34]:

$$\rho = |\psi|^2, \quad \text{with} \quad \psi(x) = a \cdot \text{sech}(b|x| + x_0), \quad (35)$$

where the parameters a, b, x_0 only depend on α and c_{xc} and are given by

$$x_0 = \text{arctanh}\left(\frac{1}{b}\right), \quad a = \sqrt{\frac{b^2}{2(b-1)}}, \quad b = 1 - \alpha \frac{1 - 2c_{xc}}{2}.$$

With this we obtain

$$I_\alpha^H + I_{2-\alpha}^H = \frac{1}{12}(\alpha^2(3 - 12c_{xc}^2) + 6\alpha(4c_{xc}^2 - 1) - 4(1 + 2c_{xc} + 4c_{xc}^2))$$

which directly implies

$$\min_{\alpha \in [0,2]} I_\alpha^H + I_{2-\alpha}^H = I_2^H.$$

Therefore for $c_{xc} > \frac{1}{2}$, we always have both electrons bound at one nucleus.

The fact that the minimum is attained at an integer, is also something we observe numerically in the 3D case. From the view point of physics this make sense since we can not split an electron in half, but it is non obvious why this drops out of the mathematics.

3.2 The three dimensional case

Now we go back to the physically more interesting case of three dimensions. Since we are just considering the H -atom the kinetic energy is the same as the von-Weizäcker kinetic energy, i.e.

$$\mathcal{E}[\rho] = \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 dx + \int_{\mathbb{R}^3} V \rho dx + J[\rho] + \int_{\mathbb{R}^3} e_{xc}(\rho) dx \quad (36)$$

and with the energy as before

$$E_\alpha = \inf_{\rho \in \mathcal{A}_\alpha} \mathcal{E}[\rho], \quad \mathcal{A}_\alpha := \{\rho \in L^1 : \sqrt{\rho} \in H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho dx = \alpha\}.$$

In this section assume the exchange functional in (36) is given by $e_{xc}(\rho) = -c_{xc}\rho^{4/3}$ (Dirac-exchange).

Then for $c_{xc} \gg 1$ we observe symmetry breaking as in the one-dimensional case.

Proposition 2 (Neutrally charged case). *For $c_{xc} = 0$ we have the correct splitting, i.e. $\alpha = 1$ is the unique global minimizer to $\alpha \mapsto E_\alpha + E_{2N-\alpha}$. On the other hand there exists a $c(N) > 0$ such that if $c_{xc} > c(N)$ we obtain*

$$2E_N > (E_\alpha + E_{2N-\alpha}) \quad \forall \alpha \neq N$$

i.e. symmetry breaking occurs.

Proof. We start with the extreme case with $c_{xc} = 0$, then the functional $\rho \mapsto \mathcal{E}[\rho]$ is strictly convex and hence we obtain for any admissible densities $\rho_\alpha, \rho_{2N-\alpha}$ with mass α and $2N - \alpha$, respectively

$$2E_N \leq 2\mathcal{E}[\frac{1}{2}\rho_\alpha + \frac{1}{2}\rho_{2N-\alpha}] < \mathcal{E}[\rho_\alpha] + \mathcal{E}[\rho_{2N-\alpha}].$$

Taking now the infimum over ρ_α and $\rho_{2N-\alpha}$ gives

$$2E_N = \min_{\alpha \in [0, N]} (E_\alpha + E_{2N-\alpha}).$$

So here the minimum is really attained at the symmetric splitting. Furthermore we also have that $\alpha = N$ is always the strict global minimizer. If minimizer exist for every $\alpha \in [0, N + \varepsilon]$ then we directly get a strong inequality $2E_N < E_\alpha + E_{2N-\alpha}$ for $\alpha \neq N$, since in this case $\alpha = N$ would be a strict local minimum and hence the global minimum. If we do not have minimizer, then this can only happen if $\alpha \mapsto E_\alpha$ is not strictly decreasing anymore for $\alpha > N$, but due to convexity and the fact that $\alpha \mapsto E_\alpha$ is monotonically decreasing, we must have $E_\alpha = E_N$ for every $\alpha \in [N, 2N]$. But in this case we have

$$E_\alpha + E_{2N-\alpha} = E_\alpha + E_N > 2E_N.$$

Now we consider the second statement, i.e. we take c_{xc} to be large. In order to see this, let ρ_N denote a minimizer of E_N and $\eta \in (0, N)$. Then

$$\begin{aligned} E_{(N+\eta)} + E_{(N-\eta)} &\leq \mathcal{E}[(1 + \frac{\eta}{N})\rho_N] + \mathcal{E}[(1 - \frac{\eta}{N})\rho_N] \\ &= 2(T[\rho_N] + V[\rho_N]) + ((1 + \frac{\eta}{N})^2 + (1 - \frac{\eta}{N})^2)J[\rho_N] + ((1 + \frac{\eta}{N})^{4/3} + (1 - \frac{\eta}{N})^{4/3})E_{xc}[\rho_N] \\ &= 2E_N + \frac{\eta^2}{N^2} \left(2J[\rho_N] + \frac{4}{9}E_{xc}[\rho_N] \right) + o(\frac{\eta^2}{N^2}), \end{aligned}$$

where we used the Taylor-expansion for $(1 \pm \eta)^{4/3}$. Now we can use Hardy-Littlewood-Sobolev and then Hölder interpolation to bound $J[\rho_N]$.

$$2J[\rho_N] = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_N(x)\rho_N(y)}{|x-y|} dx dy \leq C_{HLS} \|\rho_N\|_{\frac{5}{3}}^2 \leq C_{HLS} \|\rho_N\|_1^{2/3} \|\rho_N\|_{4/3}^{4/3}.$$

So we get using $\|\rho_N\|_1 = N$

$$2J[\rho_N] + \frac{4}{9}E_{xc}[\rho_N] \leq \left(C_{HLS}N^{2/3} - \frac{4}{9}c_{xc} \right) \int_{\mathbb{R}^3} \rho_1^{4/3} dx < 0,$$

for $c_{xc} > \frac{9}{4}C_{HLS}N^{2/3}$. Putting in the numbers, i.e. using the optimal C_{HLS} given in [20] we see that

$$c_{xc} > \frac{9}{4}\sqrt{\pi} \frac{\Gamma(1)}{\Gamma(\frac{5}{2})} \left(\frac{\Gamma(3)}{\Gamma(\frac{3}{2})} \right)^{2/3} N^{2/3} \approx 5.1615 N^{2/3}$$

suffices. In this case the symmetric splitting of the mass is not the minimum, in fact it is the maximum since the remaining terms in the Taylor expansion all have negative sign. \square

While Proposition 2 deals with the extreme cases $c_{xc} = 0$ and $c_{xc} \gg 1$, we were not able to prove symmetric splitting for the physically most interest case $c_{xc} = \frac{3}{4}(\frac{3}{\pi})^{1/3}$. Therefore, we studied the behavior numerically. As in the one-dimensional setting 3.1, the minimum seems to be always attained at an integer pair. But the transition from symmetric to asymmetric seems to be more interesting since the function $\lambda \mapsto I_\lambda^H + I_{2-\lambda}^H$ does not simply switch from convex to concave.

The computations for Figures 2 and 3 were done using the OCTOPUS package [2]. We remark that after rescaling to an L^2 normalized orbital, I_λ^H can be computed from a more standard DFT problem with modified electron-electron interaction potential (fractional charge) and modified exchange constant (cp. Slater X- α exchange).

If we already start with a positively charged molecule in the beginning and thus wonder about the minimum of $\alpha \mapsto E_{2\lambda-\alpha} + E_\alpha$ for $\lambda < N$ we can get a stronger result.

Proposition 3 (Positively charged case). *Let $\lambda < N$, then there exists a constant $c(\lambda) > 0$ such that for all $c_{xc} < c(\lambda)$ we have*

$$\min_{\alpha \in [0, \lambda]} (E_{2\lambda-\alpha} + E_\alpha) = 2E_\lambda.$$

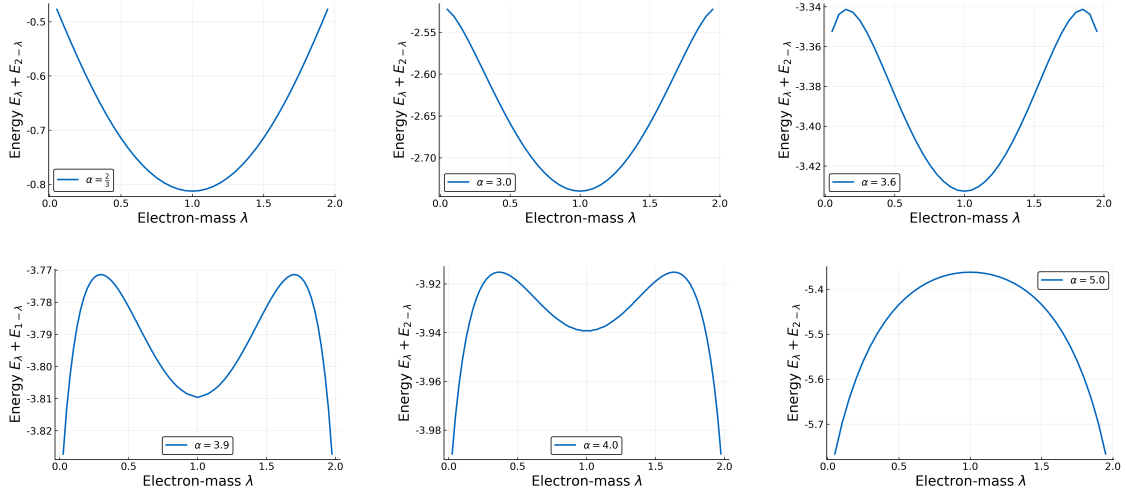


Figure 2: The function $\lambda \mapsto I_\lambda^H + I_{2-\lambda}^H$ for increasing values of c_{xc}

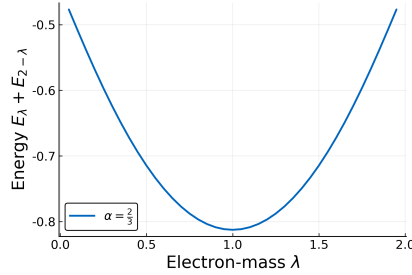


Figure 3: For the standard choice of the constant $c_{xc} = \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3}$ we get numerically the right dissociation.

Proof. As in the proof of Proposition 2 we know that for $c_{xc} = 0$ the symmetric splitting is the strict global minimum. By continuity it thus suffices to show that it stays a local one for all c_{xc} small enough.

This follows quite straightforward by result of Le Bris [19], where he proved that the mapping $\alpha \mapsto E_\alpha$ is strictly convex for $\alpha \leq Z$ and $c_{xc} > 0$ small enough. This directly implies

$$2E_\lambda < E_{\lambda-\alpha} + E_{\lambda+\alpha}, \quad \forall \alpha \in (0, Z - \lambda).$$

□

Remark. Note that Le Bris originally proved his convexity result for the Thomas-Fermi-Dirac-Von Weizsäcker model. But since he considered an arbitrary non-negative constant in front of the Thomas-Fermi term, this reduces to our model in the hydrogen case, if we set this constant to zero.

4 Dissociation limit – The proof

This section contains the proof to Theorem 1, it is split into two parts containing the upper bound and lower bound, respectively.

4.1 Upper bound

We begin by proving the upper bound to Theorem 1, i.e.

$$\limsup_{R \rightarrow \infty} I_{\lambda, R}^{X_2} \leq \min_{\alpha \in [0, \frac{\lambda}{2}]} (I_\alpha^X + I_{\lambda-\alpha}^X). \quad (37)$$

For this purpose, given $\varepsilon > 0$ take $\gamma_\alpha \in K_\alpha$ and $\gamma_{\lambda-\alpha} \in K_{\lambda-\alpha}$, s.t.

$$\mathcal{E}[\gamma_\alpha] \leq I_\alpha^H + \frac{\varepsilon}{2} \quad \text{and} \quad \mathcal{E}[\gamma_{\lambda-\alpha}] \leq I_{\lambda-\alpha}^H + \frac{\varepsilon}{2}.$$

Thanks to the continuity of the energy functionals established in Lemma 2 and the fact that the finite rank operator and the functions $C_c^\infty(\mathbb{R}^3)$ are dense in \mathcal{H} and $L^2(\mathbb{R}^3)$, respectively, we may assume that both γ_α and $\gamma_{\lambda-\alpha}$ have finite rank with range in $C_c^\infty(\mathbb{R}^3)$.

Then define the operator $\gamma_R := \gamma_\alpha + \tau_R \gamma_{\lambda-\alpha} \tau_{-R}$, where τ_R is the unitary operator on $L^2(\mathbb{R}^3)$ defined by

$$(\tau_R f)(x) := f(x - R).$$

For R large enough we have $\gamma_R \in K_\lambda$ and thus

$$\begin{aligned} I_{\lambda, R}^{X_2} &\leq \mathcal{E}_R^{X_2}[\gamma_R] \\ &\leq \mathcal{E}^X[\gamma_\alpha] + \mathcal{E}^X[\gamma_{\lambda-\alpha}] + \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\gamma_{\lambda-\alpha}}(x-R) \rho_{\gamma_\alpha}(y)}{|x-y|} dx dy \\ &\leq I_\alpha^X + I_{\lambda-\alpha}^X + \varepsilon + \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\gamma_{\lambda-\alpha}}(x-R) \rho_{\gamma_\alpha}(y)}{|x-y|} dx dy \xrightarrow{R \rightarrow \infty} I_\alpha^X + I_{\lambda-\alpha}^X + \varepsilon \end{aligned}$$

Taking the limsup yields

$$\limsup_{R \rightarrow \infty} I_{\lambda, R}^{X_2} \leq I_\alpha^X + I_{\lambda-\alpha}^X + \varepsilon.$$

Since $\varepsilon > 0$ and also $\alpha \in [0, \lambda]$ were arbitrary, we get the desired assertion.

4.2 Lower bound

The lower bound is more difficult, we want to prove

$$\liminf_{R \rightarrow \infty} I_{\lambda, R}^{X_2} \geq \min_{\alpha \in [0, \lambda]} (I_\alpha^X + I_{\lambda-\alpha}^X). \quad (38)$$

Our proof idea is to use the concentration-compactness lemma, which is usually applied to a minimizing sequence, but this time act on a sequence of minimizers $(\gamma_{R_n})_n$ of $I_{\lambda, R_n}^{X_2}$ for a sequence $(R_n)_n$ tending to infinity.

In the following we will denote the arising subsequence also with $(\gamma_{R_n})_n$ to keep notation clearer. Furthermore in the following $C > 0$ will denote a generic constant, which may have different values at each appearance, indicating some finite positive constant independent of the surrounding variables.

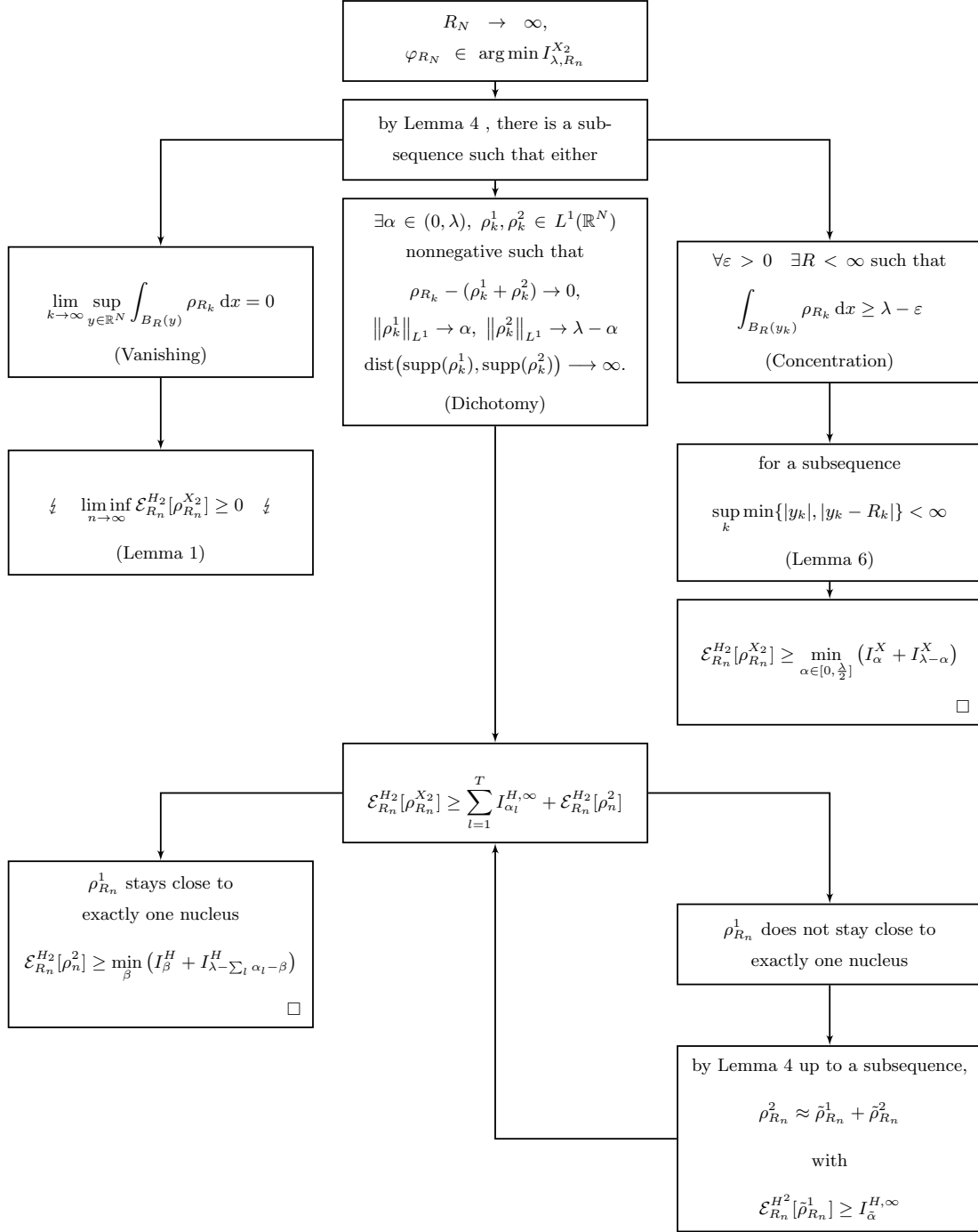


Figure 4: Structure of the proof for the lower bound. The loop on the bottom-right can only be visited a finite number of times.

Lemma 4 (Lions [22]). *Let $(\rho_n)_{n \geq 1} \subseteq L^1(\mathbb{R}^N)$ be a sequence of nonnegative functions such that*

$$\int_{\mathbb{R}^N} \rho_n \, dx = \lambda, \quad \lambda > 0 \text{ fixed.}$$

Then there exists a subsequence $(\rho_{n_k})_{k \geq 1}$ satisfying one (and only one) of the following properties:

1. **Concentration** *There is $(y_{n_k})_{k \geq 1} \subseteq \mathbb{R}^N$ such that $\rho(\cdot + y_{n_k})$ is tight, i.e.*

$$\forall \varepsilon > 0 \quad \exists R < \infty : \int_{B_R(y_k)} \rho_{n_k} \, dx \geq \lambda - \varepsilon$$

2. **Vanishing** *For any $R < \infty$, we have*

$$\lim_{k \rightarrow \infty} \sup_{y \in \mathbb{R}^N} \int_{B_R(y)} \rho_{n_k} \, dx = 0,$$

3. **Dichotomy** *There is $\alpha \in (0, \lambda)$ and $\rho_k^1, \rho_k^2 \in L^1(\mathbb{R}^N)$ nonnegative such that*

$$\begin{aligned} \int_{\mathbb{R}^N} |\rho_{n_k} - \rho_k^1 - \rho_k^2| &\longrightarrow 0, \\ \int_{\mathbb{R}^N} \rho_k^1 &\longrightarrow \alpha \text{ and } \int_{\mathbb{R}^N} \rho_k^2 \longrightarrow \lambda - \alpha \\ \text{dist}(\text{supp}(\rho_k^1), \text{supp}(\rho_k^2)) &\longrightarrow \infty. \end{aligned}$$

For the dichotomy case we will actually use the stronger statement given in [23] see below.

Hence we have to distinguish three cases. Note that case 2. and 3. correspond to the same thing, i.e. the electron mass is distributed over the two nuclei. The concentration case is only the extreme case where the entire mass stays at one nucleus.

Therefore let us start with the vanishing case.

Case 1: **Vanishing**:

We apply the bounds for the energy functional \mathcal{E}^{X_2} established in (3), which yields

$$\left\| \nabla \sqrt{\rho_{R_n}^{X_2}} \right\| \leq C + \mathcal{E}^{X_2}[\rho_{R_n}^{X_2}] = C + I_{\lambda, R_n}^{X_2} \leq C,$$

which implies that the sequence $(\rho_{R_n}^{X_2})_n$ is bounded in $H^1(\mathbb{R}^3)$. Hence we can apply the following lemma by Lions.

Lemma 5 (P.-L. Lions [23]). *Let $1 \leq p \leq \infty$, $1 \leq q < \infty$ with $q \neq \frac{Np}{N-p} =: p^*$ if $p < N$. Assume that $(u_n)_{n \geq 1}$ and $(\nabla u_n)_n$ are bounded in $L^q(\mathbb{R}^N)$ and $L^p(\mathbb{R}^N)$, respectively. If*

$$\sup_{y \in \mathbb{R}^N} \int_{B_R(y)} |u_n|^q \, dx \xrightarrow{n \rightarrow \infty} 0, \quad \text{for some } R > 0,$$

then $u_n \rightarrow 0$ in $L^\alpha(\mathbb{R}^N)$ for α between q and p^ (if $p \geq N$ set $p^* = \infty$).*

With $p = q = 2$ we obtain that

$$\sqrt{\rho_{R_n}^{X_2}} \xrightarrow{n \rightarrow \infty} 0, \quad \text{in } L^\alpha(\mathbb{R}^3), \quad \alpha \in (2, 6).$$

So clearly we get

$$E_{xc}[\rho_{R_n}^{X_2}] = -c_{xc} \int_{\mathbb{R}^3} (\rho_{R_n}^{X_2})^{4/3} dx \xrightarrow{n \rightarrow \infty} 0.$$

Furthermore we can split the Coulomb potential $V = v_1 + v_2$ with $v_1 \in L^q(\mathbb{R}^3)$ and $v_2 \in L^r(\mathbb{R}^3)$ with $\frac{3}{2} < r, q < \infty$. Hence by applying Hölder inequality we obtain

$$\left| \int_{\mathbb{R}^3} \frac{1}{|x|} \rho_{R_n}^{X_2} dx \right| \leq \|v_1\|_q \|\rho_{R_n}^{X_2}\|_{q'} + \|v_2\|_r \|\rho_{R_n}^{X_2}\|_{r'} \xrightarrow{n \rightarrow \infty} 0.$$

Analogously for the second nucleus with Coulomb potential $\frac{1}{|\cdot - R_n|}$. So combining those two results yields

$$\liminf_{n \rightarrow \infty} \mathcal{E}^{X_2, R_n}[\rho_{R_n}^{X_2}] \geq 0,$$

but this contradicts the upper bound (37) we established

$$0 \leq \liminf_{n \rightarrow \infty} \mathcal{E}^{X_2, R_n}[\rho_{R_n}^{X_2}] \leq \limsup_{n \rightarrow \infty} \mathcal{E}^{X_2, R_n}[\rho_{R_n}^{X_2}] \leq \min_{\alpha \in [0, \frac{1}{2}]} (I_\alpha^X + I_{\lambda - \alpha}^X) < 0 \quad \not\leq.$$

Therefore Vanishing cannot occur.

Case 2: Concentration: Assume concentration occurs, i.e.

$$\forall \varepsilon > 0 \exists (y_n)_n, M < \infty : \int_{B_M(y_n)} \rho_{R_n}^{X_2}(x) dx \geq \lambda - \varepsilon \quad \forall n.$$

Intuitively this corresponds to

$$\mathcal{E}[\rho_{R_n}^{X_2}] \xrightarrow{n \rightarrow \infty} I_\lambda^H + I_0^H = I_\lambda^H.$$

We start off with a small lemma.

Lemma 6. *The sequence $(y_n)_n$ stays bounded around 0 or $(R_n)_n$, to be more precise (up to a subsequence)*

$$\exists L < \infty \quad \forall n \geq 0 : |y_n| \leq L \text{ or } |y_n - R_n| \leq L.$$

Proof. Assume $|y_n| > L$ and $|y_n - R_n| > L$ for any $L > 0$ (in particular $L \gg M$). We estimate the Coulomb interaction by applying Cauchy-Schwarz and then Hardy's inequality to obtain

$$\begin{aligned} \int \frac{\rho_{R_n}^{X_2}}{|x|} dx &= \int \frac{\sqrt{\rho_{R_n}^{X_2}} \sqrt{\rho_{R_n}^{X_2}}}{|x|} dx \leq \left(\int \rho_{R_n}^{X_2} dx \right)^{1/2} \left(\int \frac{\rho_{R_n}^{X_2}}{|x|^2} dx \right)^{1/2} \\ &\leq 2 \left(\int \rho_{R_n}^{X_2} dx \right)^{1/2} \left(\int |\nabla \sqrt{\rho_{R_n}^{X_2}}|^2 dx \right)^{1/2} \leq C \left(\int \rho_{R_n}^{X_2} dx \right)^{1/2}, \end{aligned}$$

where we used that the H^1 -seminorm of $(\sqrt{\rho_{R_n}^{X_2}})_n$ stays bounded. Now if $|y_n| > L$ we obtain

$$\left(\int_{B_{L-M}(0)} \frac{\rho_{R_n}^{X_2}}{|x|} dx \right)^2 \leq C \int_{B_{L-M}(0)} \rho_{R_n}^{X_2} dx \leq C \left(\lambda - \int_{B_M(y_n)} \rho_{R_n}^{X_2} dx \right) \leq C\varepsilon$$

and the analogous result for the Coulomb interaction with the other nucleus.

Then,

$$\begin{aligned}
-V_{R_n}^{X_2}[\rho_{R_n}^{X_2}] &= \int_{\mathbb{R}^3} \rho_{R_n}^{X_2} \left(\frac{1}{|x|} + \frac{1}{|x-R|} \right) dx \\
&= \int_{B_{L-M}(0)} \frac{\rho_{R_n}^{X_2}}{|x|} dx + \int_{B_{L-M}(R_n)} \frac{\rho_{R_n}^{X_2}}{|x-R_n|} dx + \int_{B_{L-M}^c(0)} \frac{\rho_{R_n}^{X_2}}{|x|} dx + \int_{B_{L-M}^c(R_n)} \frac{\rho_{R_n}^{X_2}}{|x-R_n|} dx \\
&\leq \frac{2\lambda}{L-M} + 2C\varepsilon^{1/2}.
\end{aligned}$$

Since this inequality holds for any $L > M$ we can take $L \rightarrow \infty$ and then $\varepsilon \rightarrow 0$, which gives

$$V_{R_n}^{X_2}[\rho_{R_n}^{X_2}] \xrightarrow{n \rightarrow \infty} 0.$$

But this would imply

$$I_\lambda^X \geq \min_{\alpha \in [0, \frac{\lambda}{2}]} (I_\alpha^X + I_{\lambda-\alpha}^X) \geq \limsup_{n \rightarrow \infty} \mathcal{E}_{R_n}^{X_2}[\rho_{R_n}^{X_2}] \geq \liminf_{n \rightarrow \infty} \mathcal{E}_{R_n}^{X_2}[\rho_{R_n}^{X_2}] = \liminf_{n \rightarrow \infty} \mathcal{E}^\infty[\rho_{R_n}^{X_2}] \geq I_\lambda^\infty,$$

in contradiction to the strict inequality in Lemma 1 (ii). This finishes the proof. \square

So Lemma 6 gives us either $|y_n| \leq L$ or $|y_n - R| \leq L$ for some $L > 0$. W.l.o.g. we can in the following assume that $|y_n| \leq L$ (otherwise transform the coordinate system by a reflection s.t. 0 gets mapped to R_n . This leaves the energy functional unchanged.)

The last step consists now in a cut-off argument.

By Lemma 3 the sequence $(\gamma_{R_n}^{X_2})_n$ stays uniformly bounded in \mathcal{H} and hence we have (up to subsequence)

$$\gamma_{R_n}^{X_2} \xrightarrow{*} \gamma^* \text{ in } \mathcal{H}, \quad \sqrt{\rho_{R_n}^{X_2}} \rightharpoonup \sqrt{\rho^*} \text{ in } H^1(\mathbb{R}^3).$$

Since we are in the concentration case and the $(y_n)_n$ stays bounded, we can choose for any $\varepsilon > 0$ a compact set $K \subseteq \mathbb{R}^3$ such that

$$\int_K \rho_{R_n}^{X_2} dx \geq \int_{B_M(y_n)} \rho_{R_n}^{X_2} dx \geq \lambda - \varepsilon.$$

Therefore we get for the limit ρ^* using convergence in L_{loc}^p

$$\|\rho^*\|_1 \geq \int_K \rho^* dx = \lim_{n \rightarrow \infty} \int_K \rho_{R_n}^{X_2} dx \geq \lambda - \varepsilon,$$

since $\varepsilon > 0$ was arbitrary we get $\|\rho\|_1 = \lambda$. Therefore $\rho_{R_n}^{X_2}$ convergences also strongly in L^1 and due to the weak convergence in H^1 also strongly in $L^p(\mathbb{R}^3)$ for $p \in [1, 3)$.

Therefore we get

$$\int_{\mathbb{R}^3} \frac{1}{|x-R_n|} \rho_{R_n}^{X_2} dx \xrightarrow{n \rightarrow \infty} 0.$$

Using now the sequential weak lower semi-continuity of T we obtain

$$\liminf_{n \rightarrow \infty} \mathcal{E}^{X_2}[\gamma_{R_n}^{X_2}] \geq \mathcal{E}^\infty[\gamma^*] - \int_{\mathbb{R}^3} \frac{1}{|x|} \rho^* dx = \mathcal{E}^X[\gamma^*] \geq I_\lambda^X = I_\lambda^X + I_0^X.$$

Case 3: Dichotomy: Take a smooth partition of unity $\xi^2 + \zeta^2 = 1$ such that

$$0 \leq \xi, \zeta \leq 1, \quad \xi(x) = 1, \text{ if } |x| \leq 1, \xi(x) = 0 \text{ if } |x| \geq 2 \quad \text{and} \quad \zeta(x) = 0, \text{ for } |x| \leq 1, \zeta(x) = 1 \text{ for } |x| \geq 2.$$

Furthermore assume

$$\|\nabla \xi\|_\infty \leq 2 \text{ and } \|\nabla \zeta\|_\infty \leq 2,$$

and consider the dilated functions $\xi_K(x) = \xi(\frac{x}{K})$ and $\zeta_K(x) = \zeta(\frac{x}{K})$. Now if we use the detailed construction of the dichotomy case given in [23] (compare also [1]), we can assume that (up to a subsequence), there exists

- $\alpha \in (0, \lambda)$
- a sequence of points $(y_n)_n \in \mathbb{R}^3$
- two increasing sequences of positive real numbers $(K_n^{(1)})_n$ and $(K_n^{(2)})_n$ such that

$$\lim_{n \rightarrow \infty} K_n^{(1)} = \infty \quad \text{and} \quad \lim_{n \rightarrow \infty} \frac{K_n^{(2)}}{2} - K_n^{(1)} = \infty$$

such that the sequences $\gamma_n^{(1)} := \xi_{K_n^{(1)}} \gamma_{R_n}^{X_2} \xi_{K_n^{(1)}}$ and $\gamma_n^{(2)} := \chi_{K_n^{(2)}} \gamma_{R_n}^{X_2} \chi_{K_n^{(2)}}$ satisfy

$$\left\{ \begin{array}{l} \rho_{\gamma_{R_n}^{X_2}} = \rho_{\gamma_n^{(1)}} \text{ on } B_{K_n^{(1)}}(y_n), \quad \rho_{\gamma_{R_n}^{X_2}} = \rho_{\gamma_n^{(2)}} \text{ on } B_{K_n^{(2)}}^c(y_n), \\ \lim_{n \rightarrow \infty} \text{tr } \gamma_n^{(1)} = \alpha, \\ \lim_{n \rightarrow \infty} \text{tr } \gamma_n^{(2)} = \lambda - \alpha, \\ \rho_{\gamma_n^{(1)}} + \rho_{\gamma_n^{(2)}} - \rho_{\gamma_{R_n}^{X_2}} \xrightarrow{n \rightarrow \infty} 0 \text{ in } L^p \text{ for all } p \in [1, 3), \\ \|\rho_{\gamma_n}\|_{L^p(B_{K_n^{(2)}}(y_n) \setminus \bar{B}_{K_n^{(1)}}(y_n))} \xrightarrow{n \rightarrow \infty} 0 \text{ in } L^p \text{ for all } p \in [1, 3), \\ \lim_{n \rightarrow \infty} \text{dist}(\text{Supp}(\rho_{\gamma_n^{(1)}}), \text{Supp}(\rho_{\gamma_n^{(2)}})) = \infty, \\ \liminf_{n \rightarrow \infty} \text{tr} [-\Delta(\gamma_n - \gamma_n^{(1)} - \gamma_n^{(2)})] \geq 0. \end{array} \right. \quad (39)$$

In terms of the energy functional this splitting gives

$$\begin{aligned} \mathcal{E}^{X_2}[\gamma_{R_n}^{X_2}] &= \mathcal{E}^\infty[\gamma_n^{(1)}] + \mathcal{E}^\infty[\gamma_n^{(2)}] + \int_{\mathbb{R}^3} \rho_{\gamma_n^{(1)}} V^{X_2} + \int_{\mathbb{R}^3} \rho_{\gamma_n^{(2)}} V^{X_2} + \int_{\mathbb{R}^3} \tilde{\rho}_n V^{X_2} \\ &\quad + \text{tr} [-\Delta(\gamma_n - \gamma_n^{(1)} - \gamma_n^{(2)})] \\ &\quad + D[\rho_{\gamma_n^{(1)}}, \rho_{\gamma_n^{(2)}}] + D[\tilde{\rho}_n, \rho_{\gamma_n^{(1)}} + \rho_{\gamma_n^{(2)}}] + J[\tilde{\rho}_n] \\ &\quad + \int_{\mathbb{R}^3} e_{xc}(\rho_{R_n}^{X_2}) - e_{xc}(\rho_{\gamma_n^{(1)}}) - e_{xc}(\rho_{\gamma_n^{(2)}}), \end{aligned}$$

where we have denoted $\tilde{\rho}_n = \rho_{R_n}^{X_2} - \rho_{\gamma_n^{(1)}} - \rho_{\gamma_n^{(2)}}$. Since $\tilde{\rho}_n$ converges to zero in $L^p(\mathbb{R}^3)$ for all $p \in [1, 3)$, we obtain

$$\int_{\mathbb{R}^3} \tilde{\rho}_n V^{X_2} + D[\tilde{\rho}_n, \rho_{\gamma_n^{(1)}} + \rho_{\gamma_n^{(2)}}] + J[\tilde{\rho}_n] \xrightarrow{n \rightarrow \infty} 0.$$

Furthermore for the Coulomb-interaction between $\rho_{\gamma_n^{(1)}}$ and $\rho_{\gamma_n^{(2)}}$ we have

$$D[\rho_{\gamma_n^{(1)}}, \rho_{\gamma_n^{(2)}}] \leq \text{dist}(\text{Supp}(\rho_{\gamma_n^{(1)}}, \rho_{\gamma_n^{(2)}}))^{-1} \left\| \rho_{\gamma_n^{(1)}} \right\|_1 \left\| \rho_{\gamma_n^{(2)}} \right\|_1 \xrightarrow{n \rightarrow \infty} 0$$

and also the difference in the exchange terms vanishes

$$\begin{aligned} & \left| \int_{\mathbb{R}^3} e_{xc}(\rho_{R_n}^{X_2}) - e_{xc}(\rho_{\gamma_n^{(1)}}) - e_{xc}(\rho_{\gamma_n^{(2)}}) \right| \\ & \leq \int_{B_{K_{2,n}}(y_n) \setminus \overline{B_{K_{1,n}}}(y_n)} |e_{xc}(\rho_{R_n}^{X_2})| + |e_{xc}(\rho_{\gamma_n^{(1)}}^H)| + |e_{xc}(\rho_{\gamma_n^{(2)}}^H)| \\ & \leq 3C \left(\left\| \rho_{R_n}^{X_2} \right\|_{L^{p_-}(B_{K_{2,n}}(y_n) \setminus \overline{B_{K_{1,n}}}(y_n))}^{p_-} + \left\| \rho_{R_n}^{X_2} \right\|_{L^{p_+}(B_{K_{2,n}}(y_n) \setminus \overline{B_{K_{1,n}}}(y_n))}^{p_+} \right) \xrightarrow{n \rightarrow \infty} 0, \end{aligned}$$

where the exponents p_{\pm} are given by $p_{\pm} = 1 + \beta_{\pm}$. Using the lim inf estimate for the kinetic energy from (39), we obtain

$$\mathcal{E}^{X_2}[\gamma_{R_n}^{X_2}] \geq \mathcal{E}^{\infty}[\gamma_n^{(1)}] + \mathcal{E}^{\infty}[\gamma_n^{(2)}] + \int_{\mathbb{R}^3} \rho_{\gamma_n^{(1)}} V^{X_2} + \int_{\mathbb{R}^3} \rho_{\gamma_n^{(2)}} V^{X_2} + \mathcal{R}(n) \quad (40)$$

with a remainder $\mathcal{R}(n) \xrightarrow{n \rightarrow \infty} 0$. The last step is to deal with the nuclei part and to go from V^{X_2} to V^X ; here we again have to distinguish three cases.

Case 1: $\rho_{\gamma_n^{(1)}}$ stays close to exactly one nucleus (w.l.o.g. the one at the origin), i.e.

$$\text{dist}(0, B_{K_n^{(1)}}(y_n)) \text{ stays bounded and } \text{dist}(R_n, B_{K_n^{(1)}}(y_n)) \xrightarrow{n \rightarrow \infty} \infty.$$

Note that this necessarily implies that $\text{dist}(0, \text{Supp}(\rho_{\gamma_n^{(2)}})) \rightarrow \infty$ due to triangle inequality. Hence,

$$\int_{\mathbb{R}^3} \rho_{\gamma_n^{(1)}} \frac{1}{|x - R_n|} dx, \int_{\mathbb{R}^3} \rho_{\gamma_n^{(2)}} \frac{1}{|x|} dx \xrightarrow{n \rightarrow \infty} 0$$

and thus taking the limit in (40) and using the continuity of $\lambda \mapsto I_{\lambda}^X$ gives

$$\liminf_{n \rightarrow \infty} I_{\lambda, R_n}^{X_2} = \liminf_{n \rightarrow \infty} \mathcal{E}^{X_2}[\gamma_{R_n}^{X_2}] \geq \liminf_{n \rightarrow \infty} \mathcal{E}^X[\gamma_n^{(1)}] + \mathcal{E}^X[\gamma_n^{(2)}] \geq I_{\alpha}^X + I_{\lambda - \alpha}^X \geq \min_{\alpha \in [0, \frac{\lambda}{2}]} (I_{\alpha}^X + I_{\lambda - \alpha}^X).$$

Case 2: $\rho_{\gamma_n^{(1)}}$ does not stay close to any of the two nuclei, i.e.

$$\text{dist}(\{0, R_n\}, \text{Supp}(\rho_{\gamma_n^{(1)}})) \xrightarrow{n \rightarrow \infty} \infty.$$

Then (40) becomes

$$\begin{aligned} \min_{\alpha \in [0, \frac{\lambda}{2}]} (I_{\alpha}^X + I_{\lambda - \alpha}^X) & \geq \liminf_{n \rightarrow \infty} \mathcal{E}^{X_2}[\gamma_{R_n}^{X_2}] \geq I_{\alpha}^{\infty} + \liminf_{n \rightarrow \infty} \left(\mathcal{E}^{\infty}[\gamma_n^{(2)}] + \int_{\mathbb{R}^3} \rho_{\gamma_n^{(2)}} V^{X_2} \right) \\ & = I_{\alpha}^{\infty} + \liminf_{n \rightarrow \infty} \mathcal{E}^{X_2}[\gamma_n^{(2)}] \\ & \geq I_{\alpha}^{\infty} + \underbrace{\liminf_{n \rightarrow \infty} \mathcal{E}^{X_2}[\tilde{\gamma}_n]}_{=: J_{\lambda - \alpha}} \end{aligned}$$

where $\tilde{\gamma}_n$ is a minimizer of the problem $I_{\lambda-\alpha, R_n}^{X_2}$ for each n .

Case 3: Here $\rho_{\gamma_n^{(1)}}$ stays close to both of the nuclei and hence $\rho_{\gamma_n^{(2)}}$ does not stay close to any of the two. Thus we get the same result as in case 2, but with α and $\lambda - \alpha$ exchanged.

So we obtain

$$J_\lambda \geq I_\alpha^{X, \infty} + J_{\lambda-\alpha} \text{ (case 2)} \quad \text{or} \quad J_\lambda \geq I_{\lambda-\alpha}^{X, \infty} + J_\alpha \text{ (case 3)},$$

and since the opposite inequality always holds we arrive at

$$J_\lambda = I_\alpha^\infty + J_{\lambda-\alpha} \text{ (case 2)} \quad \text{or} \quad J_\lambda = I_{\lambda-\alpha}^\infty + J_\alpha \text{ (case 3)}. \quad (41)$$

Note also that the part splitting off to infinity (i.e. $\gamma_n^{(1)}$ in case 2 and $\gamma_n^{(2)}$ in case 3) is almost a minimizing sequence for the problem at infinity (I_α^∞ in case 2 and $I_{\lambda-\alpha}^\infty$ in case 3) in the sense that

$$\lim_{n \rightarrow \infty} \mathcal{E}^\infty[\gamma_n^{(1)}] = I_\alpha^\infty \quad \text{and} \quad \lim_{n \rightarrow \infty} \text{tr}[\gamma_n^{(1)}] = \alpha.$$

Now we are in the same position as in the beginning of the proof: We have a sequence $\tilde{\gamma}_n$ of minimizers to the functional $\mathcal{E}_{R_n}^{X_2}$ but now with the mass constraint

$$\|\rho_{X_2}\| = \lambda - \alpha < \lambda \leq N. \quad (42)$$

Going through the entire procedure of the proof again, it either ends after a finite amount of steps (*i*) or we always end up into the dichotomy case and there case 2 or 3 (*ii*) compare Figure 4.

Case (i): After a finite amount of steps we get

$$J_\lambda \geq \sum_{l=1}^T I_{\alpha_l}^\infty + J_{\lambda - \sum_{l=1}^T \alpha_l} \geq \sum_{l=1}^T I_{\alpha_l}^\infty + \min_{\beta} (I_\beta^X + I_{\lambda-\beta - \sum_{l=1}^T \alpha_l}^X). \quad (43)$$

Let the minimum at the right hand side be attained at $\tilde{\beta}$, then we can just apply the weak subadditivity inequality from Lemma 1 to obtain the desired assertion

$$(43) = \sum_{l=1}^T I_{\alpha_l}^\infty + I_{\tilde{\beta}}^X + I_{\lambda-\tilde{\beta} - \sum_{l=1}^T \alpha_l}^X \geq I_{\tilde{\beta}}^X + I_{\lambda-\tilde{\beta}}^X \geq \min_{\alpha \in [0, \frac{\lambda}{2}]} (I_\alpha^X + I_{\lambda-\alpha}^X).$$

Case (ii): This case is the more intricate one.

After the first splitting we have for the sequence $\tilde{\gamma}_n$ that $\|\rho_{\tilde{\gamma}_n}\|_1 = \lambda - \alpha < \lambda$. In order to show that such a splitting can not occur infinitely many times we start with considering the Euler-Lagrange equations of the system.

Lemma 7 (Euler-Lagrange equations). *Let γ_R be a minimizer to the energy functional $\mathcal{E}_R^{X_2}$ to the mass constraint $\text{tr}[\gamma_R] = \lambda$ then it satisfies the Euler-Lagrange equations*

$$\gamma_R = \mathbb{1}_{(-\infty, \varepsilon_F)}(h_{\gamma_R}) + \delta, \quad \text{with } 0 \leq \delta \subset \text{Ker}(h_{\gamma_R} - \varepsilon_F) \quad (44)$$

for some $\varepsilon_F < 0$ called the Fermi energy, and with the Hamiltonian

$$h_{\gamma_R} = \left(-\frac{1}{2} \Delta + \rho_{\gamma_R} * \frac{1}{|x|} + V_R^{X_2} + e'_{xc}(\rho_{\gamma_R}) \right).$$

Furthermore, we have

$$\gamma_R \in \arg \min \{ \text{tr}[h_{\gamma_R} \gamma] : \gamma \in K_\lambda \}. \quad (45)$$

Proof. This is a standard result, but let us shortly proof it (for a more detailed version see [13]). If γ_R is a minimizer for $\mathcal{E}_R^{X_2}$ with $\text{tr}[\gamma_R] = \lambda$ we have for any $\gamma \in K_\lambda$ the inequality $\mathcal{E}_R^{X_2}[t\gamma + (1-t)\gamma_R] \geq \mathcal{E}_R^{X_2}[\gamma_R]$. In particular

$$\left. \frac{\partial}{\partial t} \mathcal{E}_R^{X_2}[t\gamma + (1-t)\gamma_R] \right|_{t=0} \geq 0. \quad (46)$$

A direct calculation leads to

$$\left. \frac{\partial}{\partial t} \mathcal{E}_R^{X_2}[t\gamma + (1-t)\gamma_R] \right|_{t=0} = \text{tr} [h_{\gamma_R}(\gamma - \gamma_R)]$$

with h_{γ_R} as above. Due to (46) we must have $\gamma_R \in \arg \min\{\text{tr}[h_{\gamma_R}\gamma] : \gamma \in K_\lambda\}$. the representation of γ_R then immediately follows. \square

Note that (45) implies that in fact only finitely many orbitals are occupied, i.e.

$$\gamma = \sum_{l=1}^n |\varphi^l\rangle\langle\varphi^l| + \sum_{l=n}^m \lambda_l |\varphi^l\rangle\langle\varphi^l|,$$

with $\lambda_l \in [0, 1]$.

Furthermore every occupied orbital φ_n^l is an eigenstate of the corresponding hamiltonian $h_{\tilde{\gamma}_n}$, i.e. satisfies

$$\left(-\frac{1}{2}\Delta + \rho_{\tilde{\gamma}_n} * \frac{1}{|x|} + V_{R_n}^{X_2} + e'_{xc}(\rho_{\tilde{\gamma}_n})\right)\varphi_n^l + \theta_n^l \varphi_n^l = 0, \quad (47)$$

where $-\theta_n^1 < -\theta_n^2 \leq \dots$ denotes the ordered eigenvalues. Our first step consist in proving that for fixed l the sequence $(\theta_n^l)_n$ stay bounded away from 0.

Lemma 8. *Denote by $(\theta_n^l)_n$ the sequence of smallest eigenvalues in (47), then we have*

$$\liminf_{n \rightarrow \infty} \theta_n^l > 0. \quad (48)$$

Proof. To see this note

$$h_{\rho_{\tilde{\gamma}_n}} \leq -\frac{1}{2}\Delta + \rho_{\tilde{\gamma}_n} * \frac{1}{|x|} + V_{R_n}^{X_2} = \tilde{h}_n,$$

so it is enough to consider the latter operator \tilde{h}_n . As in [24] consider a radially symmetric function $\psi \in C_c^\infty$ with $\|\psi\|_2 = 1$ and set $\psi_\sigma = \sigma^{3/2}\psi(\sigma\cdot)$. Then we get

$$\langle \psi_\sigma, \tilde{h}_n \psi_\sigma \rangle = \frac{1}{\sigma} \int_{\mathbb{R}^3} |\nabla \psi|^2 dx + \frac{1}{\sigma} \int_{\mathbb{R}^3} V_\sigma(x) |\psi|^2 dx + \frac{1}{\sigma} \int_{\mathbb{R}^3} \left(\rho_{\sigma, \tilde{\gamma}_n} * \frac{1}{|x|} \right) |\psi|^2 dx,$$

where $V_\sigma = -\frac{Z}{|x|} - \frac{Z}{|x - \frac{R_n}{\sigma}|}$ and $\rho_{\sigma, \tilde{\gamma}_n} = \sigma^3 \rho_{\tilde{\gamma}_n}(\sigma\cdot)$. Due to radial symmetry we have

$$\begin{aligned} \int_{\mathbb{R}^3} \left(\rho_{\sigma, \tilde{\gamma}_n} * \frac{1}{|x|} \right) |\psi|^2 dx &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\psi|^2(y)}{\max\{|x|, |y|\}} dy \rho_{\tilde{\gamma}_n}(x) dx \\ &\leq \underbrace{\|\rho_{\tilde{\gamma}_n}\|_1}_{\lambda - \alpha} \int_{\mathbb{R}^3} \frac{|\psi|^2(y)}{|y|} dy. \end{aligned}$$

By Rayleigh-Ritz we thus have for every fixed n taking $\sigma \rightarrow \infty$

$$-\theta_n^1 = \inf \langle \psi, h_{\rho_{\tilde{\gamma}_n}} \psi \rangle \leq \inf \langle \psi, \tilde{h}_n \psi \rangle \leq \underbrace{(\lambda - \alpha - 2Z)}_{<0} \int_{\mathbb{R}^3} \frac{|\psi|^2(y)}{|y|} dy,$$

where the right hand side is independent of n . For $l > 1$ simply take a family of orthogonal functions $(\psi_j)_{j=1}^k$ with the same properties as ψ above, the min-max principle then gives the result. \square

Since also for $\tilde{\gamma}_n$ the dichotomy case occurs we get $\tilde{\gamma}_n^{(1)}$ and $\tilde{\gamma}_n^{(2)}$ with the same properties as listed in (39). Define $\omega_n^l := (1 - \xi_{K_n^{(1)}} - \chi_{K_n^{(2)}})\varphi_n^l = \varepsilon_n \varphi_n^l$ and $\varphi_{1,n}^l = \xi_{K_n^{(1)}}\varphi_n^l, \varphi_{2,n}^l = \chi_{K_n^{(2)}}\varphi_n^l$. Note that $0 \leq \varepsilon_n \leq 1$ and $\|\nabla \varepsilon_n\|_\infty \rightarrow 0$. Furthermore we have

$$\rho_{\tilde{\gamma}_n^{(i)}} = \sum_l \lambda_l^{(n)} |\varphi_{i,n}^l|^2,$$

where $0 \leq \lambda_l^{(n)} \leq 1$ is the occupation number of the l^{th} orbital. By multiplying (47) with ω_n^l , we obtain

$$\int_{\mathbb{R}^3} \nabla \omega_n^l \cdot \nabla \varphi_n^l dx \xrightarrow{n \rightarrow \infty} 0.$$

Since $\nabla \omega_n^l = \varepsilon_n \nabla \varphi_n^l + \varphi_n^l \nabla \varepsilon_n$ and $\varepsilon_n^2 \leq \varepsilon_n$ we also get

$$\int_{\mathbb{R}^3} \varepsilon_n^2 |\nabla \varphi_n^l|^2 dx \xrightarrow{n \rightarrow \infty} 0,$$

which finally implies $\nabla \omega_n^l \rightarrow 0$ in $L^2(\mathbb{R}^3)$. Combining this with the fact that the supports of $\varphi_{1,n}^l$ and $\varphi_{2,n}^l$ go infinitely far apart for $n \rightarrow \infty$ (47) becomes

$$\left(-\frac{1}{2} \Delta + \rho_{\tilde{\gamma}_n^{(1)}} * \frac{1}{|x|} + V_{R_n}^{X_2} + e'_{xc}(\rho_{\tilde{\gamma}_n^{(1)}})\right) \varphi_{1,n}^l + \theta_n^l \varphi_{1,n}^l \xrightarrow{H^{-1}} 0 \quad (49)$$

$$\left(-\frac{1}{2} \Delta + \rho_{\tilde{\gamma}_n^{(2)}} * \frac{1}{|x|} + V_{R_n}^{X_2} + e'_{xc}(\rho_{\tilde{\gamma}_n^{(2)}})\right) \varphi_{2,n}^l + \theta_n^l \varphi_{2,n}^l \xrightarrow{H^{-1}} 0 \quad (50)$$

Note here that the eigenvalues θ_n^l are the ones from $h_{\tilde{\gamma}_n}$ and that the support of one of the two sequences drifts infinitely far way of both nuclei. W.l.o.g. let it be $\tilde{\gamma}_n^{(1)}$, then

$$\text{dist}(\{0, R_n\}, \rho_{\tilde{\gamma}_n^{(1)}}) \xrightarrow{n \rightarrow \infty} \infty$$

and since $\tilde{\gamma}_n^{(1)}$ is almost a minimizing sequence to I_α^∞ (compare above), it cannot vanish. Therefore there exists $\kappa, M > 0$ and a sequence $(y_n)_n$ of points in \mathbb{R}^3 such that

$$\int_{B_M(y_n)} \rho_{\tilde{\gamma}_n^{(1)}}(x) dx \geq \kappa > 0. \quad (51)$$

Furthermore we necessarily have

$$\text{dist}(\{0, R_n\}, (y_n)_n) \xrightarrow{n \rightarrow \infty} \infty$$

and thus (49) becomes for the translated density matrix $\tilde{\gamma}_n^{(1)} := \tau_{y_n} \tilde{\gamma}_n^{(1)} \tau_{-y_n}$ with orbitals $\tilde{\varphi}_{1,n}^l$

$$\left(-\frac{1}{2}\Delta + \rho_{\tilde{\gamma}_n^{(1)}} * \frac{1}{|x|} + e'_{xc}(\rho_{\tilde{\gamma}_n^{(1)}})\right)\tilde{\varphi}_{1,n}^l + \theta_n^l \tilde{\varphi}_{1,n}^l \xrightarrow{H^{-1}, n \rightarrow \infty} 0.$$

Finally note that $\sqrt{\rho_{\tilde{\gamma}_n^{(1)}}} \rightharpoonup \sqrt{\rho} \neq 0$ in $H^1(\mathbb{R}^3)$ due to (51).

Now if our procedure never stops we can as in [1] construct an infinity of sequences $(\varphi_{k,n}^l)_{n \in \mathbb{N}}$ such that for every $k \in \mathbb{N}$

$$\left\{ \begin{array}{l} \forall n \in \mathbb{N}, \psi_{l,k,n} := (\sqrt{\lambda_l^{(n)}} \varphi_{k,n}^l), \sqrt{\rho_{\gamma_n^{(k)}}} \text{ bounded in } H^1(\mathbb{R}^3), \int_{\mathbb{R}^3} \rho_{\gamma_n^{(k)}} = \alpha_k, \rho_{\gamma_n^{(k)}} = \sum_l |\psi_{l,k,n}|^2 \\ \left(-\frac{1}{2}\Delta + \rho_{\gamma_n^{(k)}} * \frac{1}{|x|} + e'_{xc}(\rho_{\gamma_n^{(k)}})\right)\psi_{l,k,n} + \theta_n^l \psi_{l,k,n} = \eta_n \xrightarrow{H^{-1}, n \rightarrow \infty} 0 \\ \psi_{l,k,n} \text{ converges to } \psi_{l,k} \text{ weakly in } H^1, \text{ strongly in } L_{loc}^p \text{ for } 2 \leq p < 6 \text{ and a.e. on } \mathbb{R}^3, \\ \sqrt{\rho_{\gamma_n^{(k)}}} \text{ converges to } \sqrt{\rho_k} \neq 0 \text{ weakly in } H^1, \text{ strongly in } L_{loc}^p \text{ for } 2 \leq p < 6 \text{ and a.e. on } \mathbb{R}^3, \end{array} \right.$$

where

$$\sum_{k \in \mathbb{N}} \alpha_k \leq \lambda - \alpha. \quad (52)$$

Note furthermore that

$$\sum_l \|\psi_{l,k,n}\|_{H^1}^2$$

stays bounded independent of k or n . Thus taking the limit $n \rightarrow \infty$ we get

$$\left(-\frac{1}{2}\Delta + \rho_k * \frac{1}{|x|} + e'_{xc}(\rho_k)\right)\psi_{l,k} + \theta^l \psi_{l,k} = 0, \quad (53)$$

where $\theta^l = \liminf_{n \rightarrow \infty} \theta_n^l > 0$. Furthermore we have

$$\rho_k = \sum_l |\psi_{l,k}|^2. \quad (54)$$

Since the mass of the $\rho_{\gamma_n^{(k)}}$ does not depend on n we obtain from (52)

$$\lim_{k \rightarrow \infty} \|\rho_k\|_1 = 0.$$

By multiplying (53) with $\psi_{l,k}$ and using assumption 1 we obtain

$$\begin{aligned} 0 &\geq \frac{1}{2} \sum_l \|\nabla \psi_{l,k}\|_2^2 + \sum_l \int_{\mathbb{R}^3} |\psi_{l,k}|^2 e'_{xc}(\rho_k) dx \\ &\geq \frac{1}{2} \sum_l \|\nabla \psi_{l,k}\|_2^2 - C \sum_l \left(\|\psi_{l,k}^2\|_{\frac{1}{1-\beta_-}} + \|\psi_{l,k}^2\|_{\frac{1}{1-\beta_+}} \right) \|\rho_k\|_1 \\ &\geq \frac{1}{2} \sum_l \|\nabla \psi_{l,k}\|_2^2 - C \|\rho_k\|_1 \underbrace{\sum_l \|\psi_{l,k,n}\|_{H^1}^2}_{< \infty}. \end{aligned}$$

Thus we obtain

$$\sum_l \|\nabla \psi_{l,k}\|_2^2 \xrightarrow{k \rightarrow \infty} 0.$$

Applying standard elliptic regularity results [12] to (53) now give us the inequality

$$\|\psi_{l,k}\|_\infty \leq C \|\psi_{l,k}\|_{H^1},$$

where the constant $C > 0$ does not depend on k and thus

$$\lim_{k \rightarrow \infty} \sum_l \|\psi_{l,k}\|_\infty^2 = 0.$$

Thus by (54) we also obtain

$$\lim_{k \rightarrow \infty} \|\rho_k\|_\infty = 0.$$

Again from (53) and from Assumptions 1 we deduce

$$\theta^l \|\psi_{l,k}\|_2^2 \leq C (\|\rho_k\|_\infty^{2\beta_-} + \|\rho_k\|_\infty^{2\beta_+}) \|\psi_{l,k}\|_2^2. \quad (55)$$

Now note that due to (45) at most N different energy levels are occupied. Thus

$$\|\psi_{l,k,n}\|_2^2 = \lambda_l^n = 0,$$

for all l corresponding to the $(N+1)^{\text{th}}$ or higher eigenvalues without counting multiplicity. Note that due to degeneracies this might not be the same as $l > N$. Therefore we directly get for those l

$$\|\psi_{l,k}\|_2 = 0.$$

Thus the mass of ρ_k is distributed among only finitely many energy levels l . Therefore for at least one fixed level l we can find up to a subsequence in k $\psi_{l,k}$ such that

$$\|\psi_{l,k}\|_2 \neq 0, \quad \forall k,$$

because otherwise we would have $\|\rho_k\|_1 = 0$. Hence (55) becomes

$$\theta^l \leq C (\|\rho_k\|_\infty^{2\beta_-} + \|\rho_k\|_\infty^{2\beta_+}) \xrightarrow{k \rightarrow \infty} 0,$$

which is a contradiction to Lemma 8.

Thus case (ii) can not happen and the proof is hence complete.

4.3 Proof of Proposition 1

For the upper bound we can take a $\varphi \in C_c^\infty(\mathbb{R})$ and consider as a testfunction for the H_2 Hamiltonian just the tensor product $\psi = \varphi \otimes \varphi(\cdot - R)$, i.e. $\psi(x, y) = \varphi(x)\varphi(y - R)$. Then we directly get

$$\begin{aligned} \lim_{R \rightarrow \infty} E_R^{H^2} &\leq \lim_{R \rightarrow \infty} \langle \psi, H_R(x, y) \psi \rangle \\ &= \lim_{R \rightarrow \infty} 2\langle \varphi, h(x)\varphi \rangle + |\varphi|^2(R) + |\varphi|^2(-R) + 2 \int \varphi(\pm y)\varphi(y - R) dy \\ &= 2\langle \varphi, h(x)\varphi \rangle, \end{aligned}$$

where we used that the last three terms vanish as soon as $R > \text{diam}(\text{supp}\varphi)$. Taking now the infimum w.r.t. φ and noting that the Hamiltonian h is continuous on $H^1(\mathbb{R})$ we get the result.

4.3.1 Lower bound

Since the electron-electron interaction is positive we directly get

$$H(x, y) \geq \tilde{h}(x) + \tilde{h}(y), \quad (56)$$

where $\tilde{h}(x) = -\frac{d^2}{dx^2} - \delta_0(x) - \delta_R(x)$. To determine the infimum over the right hand side, we can just consider tensor-products of functions due to the additive structure. Hence we only need to consider

$$\langle \varphi, \tilde{h}(x)\varphi \rangle, \quad \varphi \in L^2(\mathbb{R}).$$

Therefore consider any arbitrary $\varphi \in H^1(\mathbb{R})$, and two cut-off functions ξ_1 and ξ_2 with

$$\xi_1^2 + \xi_2^2 = 1, \quad \xi_1(x) = 1 \text{ for } x \leq \frac{1}{3}, \quad \xi_1(x) = 0 \text{ for } x \geq \frac{2}{3}.$$

Defining then

$$\varphi_i = \xi_i\left(\frac{\cdot}{R}\right)\varphi,$$

gives with a straightforward calculation

$$\begin{aligned} \langle \varphi, \tilde{h}(x)\varphi \rangle &\geq \langle \varphi, h_0(x)\varphi \rangle + \langle \varphi, h_R(x)\varphi \rangle + o(1) \\ &\geq \varepsilon \left(\|\varphi_1\|_2^2 + \|\varphi_2\|_2^2 \right) + o(1) = \varepsilon \|\varphi\|_2^2 + o(1), \end{aligned}$$

where we used that the lowest eigenvalue $\varepsilon = E^H$ of $h(x)$ does not depend on the position of the single nucleus in the system.

Combining this lower bound with (56) directly gives the desired assertion.

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References

- [1] A. Anantharaman and E. Cancès. Existence of minimizers for Kohn–Sham models in quantum chemistry. In *Annales de l'Institut Henri Poincaré (C) Non Linear Analysis*, volume 26, pages 2425–2455. Elsevier, 2009.
- [2] X. Andrade, D. Strubbe, U. De Giovannini, A. H. Larsen, M. J. T. Oliveira, J. Alberdi-Rodriguez, A. Varas, I. Theophilou, N. Helbig, M. J. Verstraete, L. Stella, F. Nogueira, A. Aspuru-Guzik, A. Castro, M. A. L. Marques, and A. Rubio. Real-space grids and the octopus code as tools for the development of new simulation approaches for electronic systems. *Phys. Chem. Chem. Phys.*, 17:31371–31396, 2015.
- [3] A.D. Becke. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A*, 38:3098–3100, Sep 1988.

- [4] A.D. Becke and M.R. Roussel. Exchange holes in inhomogeneous systems: A coordinate-space model. *Phys. Rev. A*, 39:3761–3767, Apr 1989.
- [5] H. Chen and G. Friesecke. Pair densities in density functional theory. *Multiscale Modeling & Simulation*, 13(4):1259–1289, 2015.
- [6] H.L. Cycon, R.G. Froese, W. Kirsch, and B. Simon. *Schrödinger Operators: With Applications to Quantum Mechanics and Global Geometry*. Springer Study Edition. Springer, 1987.
- [7] E. Davidson. *Reduced density matrices in quantum chemistry*. Academic Press, New York, 1976.
- [8] R.L. Frank, E.H. Lieb, R. Seiringer, and H. Siedentop. Müller’s exchange-correlation energy in density-matrix-functional theory. *Phys. Rev. A*, 76:052517, November 2007.
- [9] G. Friesecke. Pair correlations and exchange phenomena in the free electron gas. *Communications in mathematical physics*, 184(1):143–171, 1997.
- [10] G. Friesecke. The multiconfiguration equations for atoms and molecules: charge quantization and existence of solutions. *Archive for rational mechanics and analysis*, 169(1):35–71, 2003.
- [11] M. Fuchs, Y.-M. Niquet, X. Gonze, and K. Burke. Describing static correlation in bond dissociation by kohn–sham density functional theory. *The Journal of Chemical Physics*, 122(9):094116, 2005.
- [12] D. Gilbarg and N. S. Trudinger. *Elliptic partial differential equations of second order*. springer, 2015.
- [13] D. Gontier. Existence of minimizers for kohn–sham within the local spin density approximation. *Nonlinearity*, 28(1):57–76, 2014.
- [14] D. Gontier, M. Lewin, and F.Q. Nazar. The nonlinear Schrödinger equation for orthonormal functions: I. Existence of ground states. *arXiv preprint arXiv:2002.04963*, 2020.
- [15] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Phys. Rev. (2)*, 136:B864–B871, 1964.
- [16] M. Holst, H. Hu, J. Lu, J.L. Marzuola, D. Song, and J. Weare. Symmetry breaking in density functional theory due to dirac exchange for a hydrogen molecule. *arXiv preprint arXiv:1902.03497*, 2019.
- [17] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev. (2)*, 140:A1133–A1138, 1965.
- [18] A. Laestadius. One-Dimensional Lieb-Oxford Bounds (arxiv preprint 1910.01925), 2019.
- [19] C. Le Bris. Some results on the thomas-fermi-dirac-von weizsäcker model. *Differential and Integral Equations*, 6(2):337–353, 1993.
- [20] E.H. Lieb. Sharp Constants in the Hardy-Littlewood-Sobolev and Related Inequalities. *Annals of Mathematics*, 118(2):349–374, 1983.
- [21] E.H. Lieb. Thomas-fermi and related theories of atoms and molecules. In *The Stability of Matter: From Atoms to Stars*, pages 259–297. Springer, 1997.

- [22] P.-L. Lions. The concentration-compactness principle in the calculus of variations. the locally compact case, part 1. *Annales de l'I.H.P. Analyse non linéaire*, 1(2):109–145, 1984.
- [23] P.-L. Lions. The concentration-compactness principle in the calculus of variations. the locally compact case, part 2. *Annales de l'I.H.P. Analyse non linéaire*, 1(4):223–283, 1984.
- [24] P.-L. Lions. Solutions of hartree-fock equations for coulomb systems. *Comm. Math. Phys.*, 109(1):33–97, 1987.
- [25] J. Lu and F. Otto. Nonexistence of a minimizer for thomas–fermi–dirac–von weizsäcker model. *Communications on Pure and Applied Mathematics*, 67, 10 2014.
- [26] R.J. Magyar and K. Burke. Density-functional theory in one dimension for contact-interacting fermions. *Physical Review A*, 70(3):032508, 2004.
- [27] M.G. Medvedev, I.S. Bushmarinov, J. Sun, J.P. Perdew, and K.A. Lyssenko. Density functional theory is straying from the path toward the exact functional. *Science*, 355(6320):49–52, 2017.
- [28] R.G. Parr and W. Young. *Density functional theory of atoms and molecules*. Oxford University Press, 1989.
- [29] J.P. Perdew, K. Burke, and M. Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett.*, 77:3865–3868, Oct 1996.
- [30] J.P. Perdew, A. Savin, and K. Burke. Escaping the symmetry dilemma through a pair-density interpretation of spin-density functional theory. *Physical Review A*, 51(6):4531, 1995.
- [31] J.P. Perdew and Y. Wang. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B*, 45:13244–13249, Jun 1992.
- [32] J.P. Perdew and A. Zunger. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B*, 23:5048–5079, May 1981.
- [33] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, and M.J. Frisch. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *The Journal of Physical Chemistry*, 98(45):11623–11627, 1994.
- [34] D. Witthaut, S. Mossmann, and H.J. Korsch. Bound and resonance states of the nonlinear schrödinger equation in simple model systems. *Journal of Physics A: Mathematical and General*, 38(8):1777, 2005.