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Existence of minimizers for Dirac-Kohn-Sham models in quantum chemistry

Long Meng*

Abstract

This article is concerned with the mathematical analysis of the Dirac-Kohn-Sham models in the local density approximation (LDA) frameworks. The difficulty is that the functional is not of class $C^{1,1}$, no critical point theory can be used to handle with this kind of problem. Nevertheless, the existence of solutions of Dirac-Kohn-Sham model can be solved in the spherical symmetric situation. And we redefine the ground state on the set of solutions. Based on an energy criteria, we can prove the existence of minimizers for positive ions.

1 Introduction

Density functional theory (DFT) of non-relativistic many particle system has progressed steadily over the last fifty years, and it has emerged as the most widely used method of electronic structure in both quantum chemistry and condensed matter physics. Akin to the Hartree-Fock approximation, the Kohn-Sham model [KS65], which relies on a representation of the density terms of single particle orbitals, is one of the most powerful tools among the DFT. However, these quantum chemical studies were restricted to rather light elements [JGP93]. When the heavier atoms are involved, it is expected that electrons located close to the nucleus will move at high velocities, thus requiring a relativistic treatment.

The relativistic density functional theory (rDFT), first laid out by A.K. Rajagopal and J. Callaway, can be rigorously derived from quantum electrodynamics [RC73,Raj78, MV79]. Then the frequently-used Dirac-Kohn-Sham model was derived by A.K. Rajagopal [Raj78] and independently by A.H. MacDonald and S.H. Vosko [MV79] after making several physically reasonable approximations. Roughly speaking, similar to the relationship between Hartree-Fock and Dirac-Fock, the Dirac-Kohn-Sham model can be obtained directly from the Kohn-Sham model by replacing Schrödinger kinetic term with Dirac kinetic term.

Based on concentration-compactness principle, the mathematical theory of Kohn-Sham model has been done in [AC09]. And then several different models were studied by different authors, see for example [AM12, EL13, Gon14, CM16, FG20].

Nevertheless, the mathematical theory of rDFT is still vague and there is no mathematical literature about it. As a critical point problems, the Dirac-Kohn-Sham model is

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indeed much more complicated than the non-relativistic one. Generally, critical point problems in quantum chemistry such as Hartree-Fock model and Dirac-Fock model can be solved by the Lions-Fang-Ghoussoub critical point method which works on a complete, C^2 -Hilbert-Riemann manifold, see [Lio87, ES99, FG92, Gho93, FG94]. Unfortunately, the functional of Dirac-Kohn-Sham model is no longer of class C^2 , and to the author's knowledge, no method in modern critical points theory can be used to handle with this kind of functional.

On the other hand, in most situations of chemical interest, the negative energy states of Dirac-Fock models and Dirac-Kohn-Sham models are neglected. Mathematically this means that one should consider the Dirac-Fock and Dirac-Kohn-Sham operator projected onto their positive spectral subspaces. Bases on these ideas, the ground energy and ground state can thus be defined on the positive spectral sub-spaces of the corresponding Dirac-Fock operator [ES01, ES02]. Then some retraction methods and fixed point theories have been introduced to handle with the problem of Dirac-Fock model, see [HS07, SER09]. Furthermore, the retraction methods utilized in [SER09] can deal with the problems lack of compactness, such as the Dirac-Fock models for crystals [CMPS20].

However, in order to use the retraction methods, the functional should be at least of class $C^{1,1}$. Unfortunately, the functional of Dirac-Kohn-Sham model is at most of class $C^{1,1/3}$ because of the exchange-correlation term and Sobolev inequality.

Nevertheless, inspired by the idea of [WOL72, Lio87], on account of the spherical symmetry the existence of solutions of Dirac-Kohn-Sham equations can be proved by using the Schauder fixed-point theorem. Thus, we define the ground state of Dirac-Kohn-Sham model on the set of solutions. Meanwhile, we found one energy criteria under which any minimizing sequence is precompact.

2 Mathematical foundations of Dirac-Kohn-Sham model and main results

2.1 Foundations of the model

In relativistic quantum mechanics, the Dirac operator can be written as

$$D^0 := -i \sum_{k=1}^3 \alpha_k \partial_k + \beta := -i \boldsymbol{\alpha} \cdot \nabla + \beta$$

where $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$ and

$$\beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix}, \quad \alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix},$$

with

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Throughout the paper, we choose units for which $m = c = \hbar = 1$, where m is the mass of the electron, c the speed of light, and \hbar the Plank constant.

The operator D^0 acts on 4-spinors, i.e. functions from \mathbb{R}^3 to \mathbb{C}^4 . And it is self-adjoint on $L^2(\mathbb{R}^3; \mathbb{C}^4)$, with domain $H^1(\mathbb{R}^3; \mathbb{C}^4)$ and form domain $H^{1/2}(\mathbb{R}^3; \mathbb{C}^4)$. Its spectrum is $\sigma(D^0) = (-\infty, -1] \cup [1, \infty)$. Moreover, it is defined to ensure

$$(D^0)^2 = -\Delta + 1.$$

Following the notation in [Tha13, ES99], we denote by Λ^+ and $\Lambda^- := \mathbb{1}_{L^2} - \Lambda^+$ respectively the two orthogonal projectors on L^2 corresponding to the positive and negative eigenspace of D^0 , and such that

$$\begin{cases} D_0\Lambda^+ = \Lambda^+D_0 = \Lambda^+\sqrt{1-\Delta} = \sqrt{1-\Delta}\Lambda^+; \\ D_0\Lambda^- = \Lambda^-D_0 = -\Lambda^-\sqrt{1-\Delta} = -\sqrt{1-\Delta}\Lambda^-. \end{cases}$$

Indeed,

$$\Lambda^+ = \frac{1}{2} + \frac{D^0}{2|D^0|}, \quad \Lambda^- = \frac{1}{2} - \frac{D^0}{2|D^0|}.$$

Even though we only consider the standard models, the density matrix is still frequently utilised. They are operators defined on trace class $\sigma_1(L^2)$. Before going further, now let us introduce some useful functional spaces and the corresponding norms:

•

$$H^\alpha := \{u \in L^2; \||D^0|^\alpha u\|_{L^2} < \infty\}$$

endowed with the norm

$$\|u\|_{H^\alpha} = \||D^0|^\alpha u\|_{L^2}.$$

•

$$\mathcal{B}(W, Y) := \left\{ L : W \rightarrow Y; \sup_{u \in W, \|u\|_W = 1} \|Lu\|_Y < \infty \right\},$$

endowed with the norm

$$\|L\|_{\mathcal{B}(W, Y)} := \sup_{u \in W, \|u\|_W = 1} \|Lu\|_Y.$$

And if $W = Y$, we also denote $\mathcal{B}(W) := \mathcal{B}(W, W)$.

•

$$X := \{\gamma \in \mathcal{B}(L^2); \gamma = \gamma^*, |D^0|^{1/2}\gamma|D^0|^{1/2} \in \sigma_1(L^2)\},$$

endowed with the norm

$$\|\gamma\|_X := \||D^0|^{1/2}\gamma|D^0|^{1/2}\|_{\sigma_1}.$$

For every density of matrix $\gamma \in X$, there exists a complete set of eigenfunctions $(u_n)_{n \geq 1}$ of γ in L^2 corresponding to the non-decreasing sequence of eigenvalues $\lambda_n \geq 0$ (counted with their multiplicity) such that $u_n \in H^{1/2}(\mathbb{R}^3, \mathbb{C}^4)$. Then the kernel $\gamma(x, y)$ of γ can be written as

$$\gamma(x, y) = \sum_{n \geq 1} \lambda_n u_n(x) u_n^*(y).$$

And the one-particle density associated with γ is

$$\rho_\gamma(x) := \text{Tr}_{\mathbb{C}^4} \gamma(x, x) = \sum_{n \geq 1} \lambda_n |u_n|^2(x).$$

Let

$$\Gamma := \{\gamma \in X; 0 \leq \gamma \leq \mathbb{1}_{L^2}\},$$

and

$$\Gamma_N := \{\gamma \in \Gamma; \text{Tr} \gamma = N\}.$$

For an atom system composed of a nucleus of charges Z ($Z \in \mathbb{N} \setminus \{0\}$ in atomic units) and N electrons, the energy of Dirac-Kohn-Sham model without considering the spin state can be written as

$$\mathcal{E}^{\text{DKS}}(Z, N)(\gamma) = \text{Tr}(D^0 \gamma) - \alpha \text{Tr}(V \gamma) + \frac{\alpha}{2} \text{Tr}(V_{\rho_\gamma} \gamma) + E_{\text{xc}}(\rho_\gamma).$$

where $\gamma \in \Gamma_N$ is the density matrix of the totally anti-symmetric wavefunction and V is the electrostatic potential generated by the nuclei defined by

$$V(x) = -\frac{Z}{|x|}.$$

In addition, V_{ρ_γ} represents the electrostatic energy of a classical charge distribution of density $\rho_\gamma(x)$

$$V_{\rho_\gamma} = \frac{1}{|\cdot|} * \rho_\gamma = \int_{\mathbb{R}^3} \frac{1}{|x-y|} \rho_\gamma(y) dy.$$

and $E_{\text{xc}}(\rho_\gamma)$ is the exchange-correlation functional of the form

$$E_{\text{xc}}(\rho_\gamma) := \int_{\mathbb{R}^3} g(\rho_\gamma)(x) dx.$$

The so-called fine structure constant α is a dimensionless positive constant (the physical value is approximately 1/137). And the corresponding Dirac-Kohn-Sham operator is defined by:

$$D_{\rho_\gamma}^{\text{DKS}}(Z) := D^0 - \alpha V + \alpha V_{\rho_\gamma} + g'(\rho_\gamma).$$

2.2 The definition of ground state

In relativistic quantum chemistry, there are three methods to define the ground state of models like (multi-configuration) Dirac-Fock: via critical point theory [ES99, Lev14], via fixed point theory [HS07], or via the retraction technique [SER09]. For the sake of critical point theory, in [Lev14] the ground state can be written as

$$E^{\text{DF}} := \min_{\Psi^+ \in \Sigma^+} \max_{\Psi^- \in (\Lambda^- H^{1/2})^N} \mathcal{E}^{\text{DF}}(g(\Psi^+ + \Psi^-)) = \min_{\Psi^+ \in \Sigma^+} \mathcal{E}^{\text{DF}}(g(\Psi^+ + h(\Psi^+))) \quad (2.1)$$

with

$$\Sigma^+ := \{\Psi^+ \in (\Lambda^+ H^{1/2})^N, \text{Gram} \Psi^+ = 1\},$$

and

$$g(\Psi) = (\text{Gram} \Psi)^{-1/2} \Psi.$$

Herein $h(\Psi^+)$ is the unique minimizer of the functional $\chi_- \in (\Lambda^- H^{1/2})^N \rightarrow \mathcal{E}^{\text{DF}}(g(\Psi^+ + \chi_-))$ because of the concavity in $(\Lambda^- H^{1/2})^N$ directions. And in order to obtain the existence of minimizers of the Dirac-Fock equation, $h(\Psi^+)$ is supposed to be of class C^1 , and \mathcal{E}^{DF} be of class C^2 .

The other methods are based on the fact that the ground state is defined on the positive spectral sub-space of the corresponding Dirac-Fock operator D_γ^{DF} [ES01, ES02]:

$$E^{\text{DF}} := \min_{\gamma \in \Gamma_{\text{DF}, N}^+} \mathcal{E}^{\text{DF}}(\gamma)$$

with

$$\Gamma_{\text{DF}, N}^+ := \{\gamma \in \Gamma; \mathbb{1}_{[0, \infty)}(D_\gamma^{\text{DF}})\gamma = \gamma, \text{Tr}_{L^2} \gamma = N\}.$$

When the fine structure constant α is small enough, the Dirac-Fock model can be regarded as a perturbed operator in terms of the unperturbed operator Dirac-Coulomb operator $D^0 + V$. Based on this idea and simple fixed point theory, Huber and Siedentop [HS07] constructed the minimizer directly.

Recently in [SER09], Séré proposed a retraction $\theta(\gamma) = \lim_{n \rightarrow \infty} T^n(\gamma)$ with

$$T(\gamma) = \mathbb{1}_{[0, \infty)}(D_\gamma^{\text{DF}})\gamma \mathbb{1}_{[0, \infty)}(D_\gamma^{\text{DF}}).$$

By the Lieb's relaxed functional and under some extra conditions for the retraction, for $N \leq Z$ the ground state can be written as

$$E^{\text{DF}} := N + \min_{\gamma \in \Gamma_{\leq, N}} (\mathcal{E}^{\text{DF}}(\theta(\gamma)) - \text{Tr}_{L^2} \theta(\gamma)),$$

with

$$\Gamma_{\text{DF}, \leq, N} := \{\gamma \in \Gamma; \text{Tr}_{L^2} \gamma \leq N\}.$$

Wherein $\theta(\gamma)$ is of class C^1 , and because of the good structure of $D\theta(\gamma)$, the minimization problem can be linearized. As a result, the existence of minimizers can be proved.

However, the energy of Dirac-Kohn-Sham model is only of class $C^{1, \alpha}$, thus we can not use the critical point theory to construct the ground state. And we can not use the Séré's retraction neither, since there is no retraction for the Dirac-Kohn-Sham models because of the exchange-correlation energy.

Nevertheless, in quantum chemistry the ground state of Dirac-Kohn-Sham model could be defined by

$$E^{\text{DKS}}(Z) := \min_{\gamma \in \Gamma_N^+} \mathcal{E}^{\text{DKS}}(Z)(\gamma)$$

with

$$\Gamma_N^+ := \{\gamma \in \Gamma; \mathbb{1}_{[0, \infty)}(D_{\rho_\gamma}^{\text{DKS}}(Z))\gamma = \gamma, \text{Tr}_{L^2} \gamma = N\}.$$

Herein, we only consider the standard Dirac-Kohn-Sham models with integer occupation numbers. If the minimizer γ_* exists, it can be written as

$$\gamma_* := \sum_{k=1}^N |u_k\rangle \langle u_k|$$

with

$$(u_k, u_l)_{L^2} = \delta_{k, l},$$

and

$$D_{\rho_\gamma}^{\text{DKS}}(Z)u_k = \nu_k u_k \quad \text{with} \quad \nu_k > 0.$$

Now for the standard Kohn-Sham models, we only need to find the minimizer in a subset of Γ_N^+ :

$$\Gamma_{\text{ps},Z,N}^+ := \left\{ \gamma \in \Gamma; \gamma = \sum_{k=1}^N |u_k\rangle \langle u_k|, (u_k, u_l)_{L^2} = \delta_{k,l}, D_{\rho_\gamma}^{\text{DKS}}(Z)u_k = \nu_k u_k \text{ with } \nu_k > 0 \right\}.$$

This set is indeed the set of solutions of Dirac-Kohn-Sham equation. Now, the ground state can be defined by

$$E^{\text{DKS}} := \inf \{ \mathcal{E}^{\text{DKS}}(\rho_\gamma)(Z), \gamma \in \Gamma_{\text{ps},Z,N}^+ \}. \quad (2.2)$$

2.3 The spherical symmetric solutions of Dirac-Kohn-Sham equation

This new definition of the ground state relies on the set of solutions of Dirac-Kohn-Sham equations. Consequently, our first aim is to prove the existence of solutions of Dirac-Kohn-Sham equations. As it has been mentioned above, it is hopeless for the author to use critical point theory to prove the existence of solutions. Inspired by the work [WOL72, Lio87], we prove the existence of solutions in the spherical symmetric situation.

Before going further, we introduce the orthonormal basis $(\Psi_{m_j, j \pm 1/2})_{(l,m,s) \in \mathcal{J}}$ of $L^2(\mathbb{S}^2)$. The C^2 functions $\Psi_{m_j, j \pm 1/2}$ are called spherical spinors and are given by

$$\Psi_{m_j, j-1/2} = \frac{1}{\sqrt{2j}} \begin{pmatrix} \sqrt{j+m_j} Y_{m_j-1/2, j-1/2} \\ \sqrt{j-m_j} Y_{m_j+1/2, j-1/2} \end{pmatrix}$$

and

$$\Psi_{m_j, j+1/2} = \frac{1}{\sqrt{2j+2}} \begin{pmatrix} \sqrt{j+1-m_j} Y_{m_j-1/2, j+1/2} \\ -\sqrt{j+1+m_j} Y_{m_j+1/2, j+1/2} \end{pmatrix}$$

where the $Y_{m,l}(\theta, \phi)$ are normalised spherical harmonics on \mathbb{S}^2 , given in terms of the associated Legendre polynomials

$$P_l^m(x) = \frac{(-1)^m}{2^l l!} (1-x^2)^{m/2} \frac{d^{m+l}}{dx^{m+l}} (x^2-1)^l$$

by

$$Y_{m,l}(\theta, \phi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} e^{im\phi} P_l^m(\cos\theta), \quad m \geq 0,$$

and

$$Y_{-m,l}(\theta, \phi) = (-1)^m \overline{Y_{m,l}(\theta, \phi)}.$$

And the set of admissible indices \mathcal{J} is defined by

$$\mathcal{J} := \left\{ (j, m_j, \kappa_j) : j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots, m_j = -j, -j+1, \dots, +j, \kappa_j = \pm(j + \frac{1}{2}) \right\}.$$

Set

$$\Phi_{m_j, \mp(j+1/2)}^+ = \begin{pmatrix} i\Psi_{m_j, j \mp 1/2} \\ 0 \end{pmatrix}, \quad \Phi_{m_j, \mp(j+1/2)}^- = \begin{pmatrix} 0 \\ \Psi_{m_j, j \pm 1/2} \end{pmatrix}.$$

There is a natural unitary isomorphism U between the Hilbert spaces $L^2(\mathbb{R}^3, \mathbb{C}^4)$ and $L^2(\mathbb{R}_+, r^2 dr) \otimes L^2(\mathbb{S}^2, \mathbb{C}^4)$, and $L^2(\mathbb{S}^2, \mathbb{C}^4)$ is the orthogonal sum of the 2-dimensional spaces $\mathfrak{H}_{m_j, \kappa_j}$ spanned by Φ_{m_j, κ_j}^+ and Φ_{m_j, κ_j}^- . Any $f \in L^2(\mathbb{S}^2, \mathbb{C}^4)$ has the representation

$$(Uf)(r, \theta, \phi) = \sum_{(j, m_j, \kappa_j) \in \mathcal{J}} (U_{m_j, \kappa_j} f)(\theta, \phi),$$

where

$$(U_{m_j, \kappa_j} f)(\theta, \phi) = r^{-1} f_{m_j, \kappa_j}^+(r) \Phi_{m_j, \kappa_j}^+(\theta, \phi) + r^{-1} f_{m_j, \kappa_j}^-(r) \Phi_{m_j, \kappa_j}^-(\theta, \phi).$$

and $f_{m_j, \kappa_j}^+, f_{m_j, \kappa_j}^- \in L^2(\mathbb{R}_+)$. And operators L may be decomposed into a direct sum of operators L_{m_j, κ_j} acting on $L^2(\mathbb{R}_+) \otimes \mathfrak{H}_{m_j, \kappa_j}$ according to

$$L_{m_j, \kappa_j}(U_{m_j, \kappa_j} f) = U_{m_j, \kappa_j}(Lf),$$

for every $f \in L^2(\mathbb{R}^3, \mathbb{C}^4)$. The operator L is then denoted by

$$L := \bigoplus_{(j, m_j, \kappa_j) \in \mathcal{J}} L_{m_j, \kappa_j}.$$

In particular, the free Dirac operator D^0 is unitary equivalent to the Dirac sum of self-adjoint operator $D^{0, l, s}$ on $L^2(\mathbb{R}_+) \otimes \mathfrak{H}_{m_j, \kappa_j}$, with

$$D^{0, m_j, \kappa_j} := \begin{pmatrix} 1 & -\frac{d}{dr} + \frac{\kappa_j}{r} \\ \frac{d}{dr} + \frac{\kappa_j}{r} & -1 \end{pmatrix} = -i\sigma_2 \frac{d}{dr} + \sigma_1 \frac{\kappa_j}{r} + \sigma_3$$

and the Dirac operator can be written as

$$D^0 = \bigoplus_{(j, m_j, \kappa_j) \in \mathcal{J}} D^{0, m_j, \kappa_j}.$$

Now for any density matrix γ with $\rho_\gamma(x) = \rho_\gamma(|x|)$, it follows from the partial wave decomposition that the relativistic Kohn-Sham operator can be written as

$$D_{\rho_\gamma}^{\text{DKS}} = \bigoplus_{(j, m_j, \kappa_j) \in \mathcal{J}} D_{\rho_\gamma}^{\text{DKS}, m_j, \kappa_j}.$$

with operator $D_{\rho_\gamma}^{\text{DKS}, m_j, \kappa_j}$ acting on $L^2(\mathbb{R}_+) \otimes \mathfrak{H}_{m_j, \kappa_j}$ and

$$D_{\rho_\gamma}^{\text{DKS}, m_j, \kappa_j}(Z) := D^{0, m_j, \kappa_j} - \frac{Z}{r} + \frac{\alpha}{r} f_{\rho_\gamma}(r) - g'_{\rho_\gamma}(r)$$

as well as

$$f_{\rho_\gamma}(r) = \int_0^r \rho_\gamma(s) ds + r \int_r^\infty \frac{\rho_\gamma(s)}{s} ds, \quad g'_{\rho_\gamma}(r) = g'(\rho_\gamma(r)).$$

From now on by virtue of the partial wave decomposition, we study the existence of solutions of the Dirac-Kohn-Sham equation in $L^2(\mathbb{R}_+) \otimes \mathfrak{H}_{m_j, \kappa_j}$, namely for $1 \leq i \leq N$

$$D_{\rho_\gamma}^{\text{DKS}, m_{j_i}, \kappa_{j_i}}(Z) u_{k_i, m_{j_i}, \kappa_{j_i}} = \lambda_{k_i, m_{j_i}, \kappa_{j_i}} u_{k_i, m_{j_i}, \kappa_{j_i}} \quad (2.3)$$

with

$$\gamma := \sum_{i=1}^N |u_{k_i, m_{j_i}, \kappa_{j_i}}\rangle \langle u_{k_i, m_{j_i}, \kappa_{j_i}}|.$$

In addition, the normalization conditions

$$(u_{k_i, m_{j_i}, \kappa_{j_i}}, u_{k_{i'}, m_{j_{i'}}, \kappa_{j_{i'}}})_{L^2} = \delta_{i, i'}, \quad \text{for } i, i' = 1, \dots, N \quad (2.4)$$

and the boundary conditions

$$u_{k_i, m_{j_i}, \kappa_{j_i}}(0) = 0 \quad (2.5)$$

must be satisfied.

The following functional spaces will be used for the above problem:

$$L^2_{m_j, \kappa_j} := L^2 \cap (L^2(\mathbb{R}_+) \otimes \mathfrak{H}_{m_j, \kappa_j}),$$

endowed with the norm

$$\|u\|_{L^2_{m_j, \kappa_j}} = \|r^{-1}u^+\Phi_{m_j, \kappa_j}^+ + r^{-1}u^-\Phi_{m_j, \kappa_j}^-\|_{L^2}.$$

for any $u := (u^+, u^-) \in L^2(\mathbb{R}_+)$. And

$$H^{\alpha}_{m_j, \kappa_j} := H^{\alpha} \cap (L^2(\mathbb{R}_+) \otimes \mathfrak{H}_{m_j, \kappa_j}),$$

with the norm

$$\|u\|_{H^{\alpha}_{m_j, \kappa_j}} := \|r^{-1}u^+\Phi_{m_j, \kappa_j}^+ + r^{-1}u^-\Phi_{m_j, \kappa_j}^-\|_{H^{\alpha}}.$$

For the convenience, we do not distinguish between $u \in L^2_{m_j, \kappa_j}$ and $u \in L^2(\mathbb{R}_+)$.

2.4 Main results

Before stating the results, we need some assumptions about the exchange-correction functional and the charges of nucleus and electron:

Assumption 2.1. The function g is a C^1 function from \mathbb{R}_+ to \mathbb{R} such that

$$g(0) = 0, \quad (2.6a)$$

$$g' \leq 0, \quad (2.6b)$$

$$\exists 0 < \beta_- \leq \beta_+ \leq \frac{1}{3} \quad \text{s.t.} \quad \sup_{\rho \in \mathbb{R}_+} \frac{|g'(\rho)|}{\rho^{\beta_-} + \rho^{\beta_+}} \leq C_{g,1}, \quad (2.6c)$$

$$\text{and} \quad \sup_{\rho \in \mathbb{R}_+} \frac{|g(\rho) - \rho g'(\rho)|}{\rho^{1+\beta_-} + \rho^{1+\beta_+}} \leq C_{g,2}, \quad (2.6d)$$

Assumption 2.2. Let $C_{\text{sob}, \beta}$ be the sharp constants for the Sobolev inequality:

$$C_{\text{sob}, \beta} := \inf_{u \in H^{3\beta/2} \setminus \{0\}} \frac{\|u\|_{H^{3\beta/2}}}{\|u\|_{L^{\frac{2}{1-\beta}}}.$$

And let $C_{\text{ex}}(N) := C_{g,1} \left(N^{\beta_+} C_{\text{sob}, \beta_+}^2 + N^{\beta_-} C_{\text{sob}, \beta_-}^2 \right)$. We assume that

- $\kappa := \frac{\pi\alpha}{2}(Z + N) + C_{\text{ex}}(N) < 1$,

- $\tau := \left(\frac{\alpha\pi}{4} N + C_{g,2} \left(C_{\text{sob},\beta_+}^2 N^{\beta_+} + C_{\text{sob},\beta_-}^2 N^{\beta_-} \right) \right) (1 - 2\alpha(Z + N) - C_{\text{ex}}(N))^{-1} < 1.$

Our method is based on the spectral analysis. The following lemma is the essential ingredient:

Lemma 2.3. *Under the Assumption 2.1 and 2.2, and assume that $0 \leq \rho$, $\|\rho\|_{L^1} = N$, $N < Z$ and \mathcal{F} is a subspace of $H^{1/2}$. There are constants $0 \leq \sigma_{\mathcal{F},k}(Z, N) \leq 1$ and $0 \leq \sigma_{\mathcal{F}}^k(Z, N) \leq 1$ independent of ρ such that the k -th eigenvalue (counted with multiplicity) of the mean-field operator $D_\rho^{\text{DKS}}(Z)$ in \mathcal{F} if it exists is situated in the interval $[\sigma_{\mathcal{F},k}(Z, N), \sigma_{\mathcal{F}}^k(Z, N)]$.*

In addition, $\sigma_{\mathcal{F},k}(Z, N), \sigma_{\mathcal{F}}^k(Z, N)$ are continuous with respect to Z and N , and non-decreasing with respect to k .

Furthermore, let $\sigma_{\mathcal{F},\text{ess}}(Z, N) = \lim_{k \rightarrow \infty} \sigma_{\mathcal{F},k}(Z, N)$ and $\sigma_{\mathcal{F}}^{\text{ess}}(Z, N) = \lim_{k \rightarrow \infty} \sigma_{\mathcal{F}}^k(Z, N)$. And let $b := \inf(\sigma_{\mathcal{F},\text{ess}}(D_\rho^{\text{DKS}}(Z))) \cap [0, \infty)$ be the bottom of the essential spectrum on the subspace \mathcal{F} . Then $b \in [\sigma_{\mathcal{F},\text{ess}}(Z, N), \sigma_{\mathcal{F}}^{\text{ess}}(Z, N)]$. And for any $\nu < \sigma_{\mathcal{F},\text{ess}}(Z, N)$, there is a constant $q \in \mathbb{Z}_+$, such that there are at most $N + q$ eigenvalues in the interval $[0, \nu]$.

For the existence of solutions, we need another assumption:

Assumption 2.4. Let $N^*(Z, N) = \max\{k \in \mathbb{Z}_+; \sigma_{H^{1/2}}^k(Z, N) \leq 1 - C_{\text{ex}}(N)\}$. We assume that

$$N \leq N^*(Z, N).$$

Now, we have the existence of solutions under the spherical symmetric condition:

Theorem 2.5. *Under Assumption 2.1, 2.2 and 2.4 there is a set $(j_i, m_{j_i}, \kappa_{j_i})_{1 \leq i \leq N} \subset \mathcal{J}$, such that there exists an orthonormal solution set $(u_{k_i, m_{j_i}, \kappa_{j_i}}, \lambda_{k_i, m_{j_i}, \kappa_{j_i}})_{1 \leq i \leq N}$ of equations 2.3 under the conditions (2.5) and (2.4). In addition, for any $1 \leq i \leq N$*

$$\sigma_{H_{m_{j_i}, \kappa_{j_i}}^{1/2}, k_i}(Z, N) \leq \lambda_{k_i, m_{j_i}, \kappa_{j_i}} \leq \sigma_{H_{m_{j_i}, \kappa_{j_i}}^{1/2}}^{k_i}(Z, N).$$

In particular, we can choose the set $(j_i, m_{j_i}, \kappa_{j_i})_{1 \leq i \leq N} \subset \mathcal{J}$ such that $\lambda_{k_i, m_{j_i}, \kappa_{j_i}}$ are the first N eigenvalues of operator $D_\rho^{\text{DKS}}(Z)$ on the space $H^{1/2}$, and

$$\sigma_{H^{1/2}, i}(Z, N) \leq \lambda_{k_i, m_{j_i}, \kappa_{j_i}} \leq \sigma_{H^{1/2}}^i(Z, N).$$

Theorem 2.6. *Under the Assumption 2.1 and Assumption 2.2, for $N < Z$, if $\Gamma_{\text{ps}, N}^+ \neq \emptyset$ and*

$$E^{\text{DKS}}(Z, N) < (1 - \tau) \left(\sum_{k=1}^{N-1} \sigma_k(Z, N) + \sigma_{\text{ess}}(Z, N) \right), \quad (2.7)$$

then the minimization problem (2.2) admits a minimizer in $\Gamma_{\text{ps}, Z, N}^+$.

Furthermore, for $N = Z$, if there is a constant $\epsilon > 0$ such that

$$[N, N + \epsilon] \subset \{Z; E^{\text{DKS}}(Z, N) < (1 - \tau) \left(\sum_{k=1}^{N-1} \sigma_k(N, N) + \sigma_{\text{ess}}(N, N) \right)\}, \quad (2.8)$$

then the minimization problem (2.2) admits a minimizer in $\Gamma_{\text{ps}, Z, N}^+$.

Remark 2.7. By analogy with the definition of ground state like Dirac-Fock by critical point theory (2.1), it is easy to see that for $Z \geq N$

$$E^{\text{DKS}}(Z, N) \leq E^{\text{DKS}}(N, N),$$

thus the condition (2.8) can be effortlessly fulfilled if $E^{\text{DKS}}(N, N) < (1-\tau)(\sum_{k=1}^{N-1} \sigma_k(N, N) + \sigma_{\text{ess}}(N, N))$.

Remark 2.8. The conditions (2.6a)-(2.6d) are obviously fulfilled by the non-relativistic LDA exchange functional, and in our system of units, $g(\rho) = -\alpha \frac{3}{4} (\frac{3}{\pi})^{1/3} \rho^{4/3}$.

3 Preliminaries

In this section, we provide some useful estimates in Dirac-Kohn-Sham models.

Lemma 3.1. *Let $\gamma \in X$. Then,*

1. For $u \in H^{1/2}$, $(u, |x|^{-1}u) \leq \frac{\pi}{2} \|u\|_{H^{1/2}}^2$ and $\|V_\gamma\|_{\mathcal{B}(L^2)} \leq \frac{\pi}{2} \|\gamma\|_X$.
2. For $u \in H^{1/2}$, and $\gamma \in \Gamma_N$,

$$(u, |g'(\rho_\gamma)|u) \leq C_{\text{ex}}(N) \|u\|_{H^{1/2}}^2, \quad (3.1)$$

where

$$C_{\text{ex}}(N) := C_{g,1} (N^{\beta_+} C_{\text{sob},\beta_+}^2 + N^{\beta_-} C_{\text{sob},\beta_-}^2),$$

Proof. For the first inequality is just the Herbst inequality. And for the second one, as $0 < \beta_- \leq \beta_+ \leq \frac{1}{3}$

$$\begin{aligned} \|(g'(\rho_\gamma))^{1/2} u\|_{L^2}^2 &\leq C_{g,1} (\|\rho_\gamma^{\beta_+/2} u\|_{L^2}^2 + \|\rho_\gamma^{\beta_-/2} u\|_{L^2}^2) \\ &\leq C_{g,1} \left(\|\rho_\gamma\|_{L^1}^{\beta_+} \|u\|_{L^{\frac{2}{1-\beta_+}}}^2 + \|\rho_\gamma\|_{L^1}^{\beta_-} \|u\|_{L^{\frac{2}{1-\beta_-}}}^2 \right) \\ &\leq C_{g,1} (N^{\beta_+} C_{\text{sob},\beta_+}^2 \| |D^0|^{3\beta_+/2} u\|_{L^2}^2 + N^{\beta_-} C_{\text{sob},\beta_-}^2 \| |D^0|^{3\beta_-/2} u\|_{L^2}^2) \\ &\leq C_{g,1} (N^{\beta_+} C_{\text{sob},\beta_+}^2 + N^{\beta_-} C_{\text{sob},\beta_-}^2) \| |D^0|^{1/2} u\|_{L^2}^2 \\ &= C_{\text{ex}}(N) \| |D^0| u\|_{L^2}^2. \end{aligned}$$

□

Now,

Lemma 3.2. *Let $\gamma \in X$. Then,*

1. If $\gamma \in \Gamma_N$, then

$$\| |D_{\rho_\gamma}|^{1/2} |D^0|^{-1/2} \|_{\mathcal{B}(L^2)} \leq (1 + \frac{\pi\alpha}{2} (Z + N) + C_{\text{ex}}(N))^{1/2},$$

and if $\gamma \in \Gamma_N$ and $\frac{\pi\alpha}{2} (Z + N) + C_{\text{ex}}(N) < 1$, then

$$\| |D^0|^{1/2} |D_{\rho_\gamma}|^{-1/2} \|_{\mathcal{B}(L^2)} \leq (1 - \frac{\pi\alpha}{2} (Z + N) - C_{\text{ex}}(N))^{-1/2}.$$

2. For $\gamma \in \Gamma_{Z,N}^+$, we have that

$$(1 - \tau) \operatorname{Tr}_{L^2}(D_{\rho_\gamma} \gamma) \leq \mathcal{E}^{\text{DKS}}(Z, N)(\gamma) \leq (1 + \tau) \operatorname{Tr}_{L^2}(D_{\rho_\gamma} \gamma)$$

where

$$\tau := \left(\frac{\alpha\pi}{4} N + C_{g,2} (C_{\text{sob},\beta_+}^2 N^{\beta_+} + C_{\text{sob},\beta_-}^2 N^{\beta_-}) \right) (1 - \frac{\pi\alpha}{2} (Z + N) - C_{ex}(N))^{-1},$$

3. If $\gamma \in \Gamma_N$, then

$$\inf |\sigma(D_{\rho_\gamma})| \geq h_0 := 1 - \max \left\{ \frac{(\pi/2 + 2/\pi)\alpha Z}{2} - \alpha C_{ex}(N), \frac{(\pi/2 + 2/\pi)\alpha N}{2} \right\}.$$

Proof. For the first estimate, as

$$|D^0| - \alpha|V| - \alpha|V_\gamma| - |g'(\rho_\gamma)| \leq |D_{\rho_\gamma}| \leq |D^0| + \alpha|V| + \alpha|V_\gamma| + |g'(\rho_\gamma)|,$$

and by the above estimate and the first estimates, we know that

$$|D_{\rho_\gamma}| \leq |D^0| + \left(\frac{\alpha\pi}{2} (Z + N) + C_{ex}(N) \right) |D^0|,$$

and

$$|D^0| - \left(\frac{\alpha\pi}{2} (Z + N) + C_{ex}(N) \right) |D^0| \leq |D_{\rho_\gamma}|.$$

Thus,

$$\| |D_{\rho_\gamma}| |D^0| \|_{\mathcal{B}(L^2)} \leq (1 + 2\alpha(Z + N) + C_{ex}(N))$$

and

$$\| |D^0| |D_{\rho_\gamma}|^{-1} \|_{\mathcal{B}(L^2)} \leq (1 - 2\alpha(Z + N) - C_{ex}(N))^{-1}.$$

Now for the estimates of the energy, note that

$$\operatorname{Tr}_{L^2} D_{\rho_\gamma} \gamma = \mathcal{E}^{\text{DKS}}(Z, N)(\gamma) + \frac{\alpha}{2} \operatorname{Tr}_{L^2}(V_\gamma \gamma) + \operatorname{Tr}_{L^2}(g'(\rho_\gamma) \gamma) - E_{ex}(\rho_\gamma).$$

By Assumption 2.1 and Gagliardo–Nirenberg interpolation inequality, we know that

$$\begin{aligned} & |\operatorname{Tr}_{L^2}(g'(\rho_\gamma) \gamma) - E_{ex}(\rho_\gamma)| \\ & \leq C_{g,2} (\|\rho_\gamma^{1+\beta_+}\|_{L^1} + \|\rho_\gamma^{1+\beta_-}\|_{L^1}) \\ & \leq C_{g,2} \left(C_{\text{sob},\beta_+}^2 \|\rho_\gamma^{1/2}\|_{L^2}^{2\beta_+} \| |D^0|^{3\beta_+/2} \rho_\gamma^{1/2} \|_{L^2}^2 + C_{\text{sob},\beta_-}^2 \|\rho_\gamma^{1/2}\|_{L^2}^{2\beta_-} \| |D^0|^{3\beta_-/2} \rho_\gamma^{1/2} \|_{L^2}^2 \right) \\ & \leq C_{g,2} (C_{\text{sob},\beta_+}^2 N^{\beta_+} + C_{\text{sob},\beta_-}^2 N^{\beta_-}) \| |D^0|^{1/2} \rho_\gamma^{1/2} \|_{L^2}^2. \end{aligned}$$

In virtue of the convexity inequality for the relativistic kinetic energy [LL01], we have that

$$|\operatorname{Tr}_{L^2}(g'(\rho_\gamma) \gamma) - E_{ex}(\rho_\gamma)| \leq C_{g,2} (C_{\text{sob},\beta_+}^2 N^{\beta_+} + C_{\text{sob},\beta_-}^2 N^{\beta_-}) \|\gamma\|_X.$$

As

$$\|V_\gamma\|_{\mathcal{B}(L^2)} \leq \frac{\pi}{2} \|\gamma\|_X,$$

we have that

$$\begin{aligned}
& |\mathrm{Tr}_{L^2} D_{\rho_\gamma} \gamma - \mathcal{E}^{\mathrm{DKS}}(Z, N)(\gamma)| \\
& \leq \left(\frac{\alpha\pi}{4} N + C_{g,2} (C_{\mathrm{sob},\beta_+}^2 N^{\beta_+} + C_{\mathrm{sob},\beta_-}^2 N^{\beta_-}) \right) \mathrm{Tr}_{L^2} |D^0| \gamma \\
& \leq \left(\frac{\alpha\pi}{4} N + C_{g,2} (C_{\mathrm{sob},\beta_+}^2 N^{\beta_+} + C_{\mathrm{sob},\beta_-}^2 N^{\beta_-}) \right) \left(1 - \frac{\pi\alpha}{2} (Z + N) - C_{ex}(N) \right)^{-1} \mathrm{Tr}_{L^2} |D_{\rho_\gamma}| \gamma.
\end{aligned}$$

Letting

$$\tau := \left(\frac{\alpha\pi}{4} N + C_{g,2} (C_{\mathrm{sob},\beta_+}^2 N^{\beta_+} + C_{\mathrm{sob},\beta_-}^2 N^{\beta_-}) \right) \left(1 - \frac{\pi\alpha}{2} (Z + N) - C_{ex}(N) \right)^{-1},$$

as $\gamma \in \Gamma_N^+$, we have that

$$(1 - \tau) \mathrm{Tr} D_{\rho_\gamma} \gamma \leq \mathcal{E}^r KS(\gamma) \leq (1 + \tau) \mathrm{Tr}_{L^2} D_{\rho_\gamma} \gamma.$$

For the last estimate, let $u^+ := \Lambda^+ u$ and $u^- := \Lambda^- u$. Now, we know that

$$\begin{cases} (u^+, D_{\rho_\gamma} u^+)_{H^{1/2} \times H^{1/2} *} \geq \left(1 - \frac{(\pi/2 + 2/\pi)\alpha Z}{2} - C_{ex}(N) \right) \|u^+\|_{H^{1/2}}^2, \\ -(u^-, D_{\rho_\gamma} u^-)_{H^{1/2} \times H^{1/2} *} \geq \left(1 - \frac{(\pi/2 + 2/\pi)\alpha N}{2} \right) \|u^-\|_{H^{1/2}}^2. \end{cases}$$

Let us choose $h_0 := 1 - \max\left\{ \frac{(\pi/2 + 2/\pi)\alpha Z}{2} - \alpha C_{ex}(N), \frac{(\pi/2 + 2/\pi)\alpha N}{2} \right\}$, we get

$$\begin{aligned}
\|u\|_{H^{1/2}} \|D_{\rho_\gamma} u\|_{H^{1/2} *} & \geq \Re(u^+ - u^-, D_{\rho_\gamma} u)_{H^{1/2} \times H^{1/2} *} \\
& = (u^+, D_{\rho_\gamma} u^+)_{H^{1/2} \times H^{1/2} *} - (u^-, D_{\rho_\gamma} u^-)_{H^{1/2} \times H^{1/2} *} \\
& \geq h_0 \|u\|_{H^{1/2}}^2.
\end{aligned}$$

□

4 Spectral analysis

proof of Lemma 2.3. As in [DES00], the definition of the k th eigenvalue if it exists can be formulated by

$$\sigma_{\mathcal{F},k}(D_\rho^{\mathrm{DKS}}(Z)) = \inf_{\substack{V \text{ subspace of } \Lambda^+ \mathcal{F} \\ \dim V = k}} \sup_{u \in (V \oplus \Lambda^- \mathcal{F}) \setminus \{0\}} \frac{(D_\rho^{\mathrm{DKS}}(Z)u, u)}{\|u\|_{L^2}^2}. \quad (4.1)$$

And if there is no k -th eigenvalue, then $\sigma_{\mathcal{F},k}(D_{\rho_\gamma}(Z))$ is the bottom of the essential spectrum. According to Newton's Theorem, we have that

$$V_\rho(x) \leq \frac{N}{|x|}.$$

Consequently,

$$\sigma_{\mathcal{F},k}(D_\rho^{\mathrm{DKS}}(Z, N)) \leq \inf_{\substack{V \text{ subspace of } \Lambda^+ \mathcal{F} \\ \dim V = k}} \sup_{u \in (V \oplus \Lambda^- \mathcal{F}) \setminus \{0\}} \frac{((D^0 - \frac{\alpha(Z-N)}{|x|})u, u)}{\|u\|_{L^2}^2} := \sigma_{\mathcal{F}}^k(Z, N).$$

Similarly, by Lemma 3.1, we know that

$$D_\rho^{\text{DKS}}(Z) \geq D^0 - \frac{\alpha Z}{|x|} - C_{ex}(N)|D^0|.$$

Thus,

$$\sigma_{\mathcal{F},k}(D_\rho^{\text{DKS}}(Z)) \geq \inf_{\substack{V \text{ subspace of } \Lambda^+ \mathcal{F} \\ \dim V = k}} \sup_{u \in (V \oplus \Lambda^- \mathcal{F}) \setminus \{0\}} \frac{((D^0 - \frac{\alpha Z}{|x|} - C_{ex}(N)|D^0|)u, u)}{\|u\|_{L^2}^2} := \sigma_{\mathcal{F},k}(Z, N).$$

For the sake of the continuity of $C_{ex}(N)$, we know that $\sigma_k(Z, N)$ and $\sigma^k(Z, N)$ are continuous with respect to Z and N . Besides, they are bounded and non-decreasing with respect to k . Thus according to the Monotone Convergence Theorem, $\sigma_{\mathcal{F},ess}(Z, N)$ and $\sigma_{\mathcal{F}}^{ess}(Z, N)$ are the unique limits of $\sigma_{\mathcal{F},k}(Z, N)$ and $\sigma_{\mathcal{F}}^k(Z, N)$ respectively. As a result, for any $\nu < \sigma_{\mathcal{F},ess}(Z, N)$, there exists a constant $q \in \mathbb{Z}_+$, such that

$$\nu < \sigma_{N+q+1}(Z, N),$$

and

$$\dim(\mathbb{1}_{[0,\nu]}(D_\rho^{\text{DKS}}(Z))) \leq N + q.$$

Furthermore, for any $k \in \mathbb{Z}_+$ such that $\sigma_{\mathcal{F},k}(D_\rho^{\text{DKS}}(Z)) < \sigma_{\mathcal{F},ess}(Z, N)$, the k -th eigenvalue of operator $D_{\rho_\gamma}^{\text{DKS}}(Z)$ exists and lies on the discrete spectrum. Thus the bottom of the essential spectrum b is situated in $[\sigma_{\mathcal{F},ess}(Z, N), \sigma_{\mathcal{F}}^{ess}(Z, N)]$.

Finally, according to [DES00] this lemma will be proved if we show that $\sigma_1(D_\rho^{\text{DKS}}(Z)) > a$ with $a := \sup_{u \in \Lambda^- H^{1/2}} \frac{(D_\rho(Z)u, u)}{\|u\|_{L^2}}$. It is obvious, since

$$\begin{aligned} & \Lambda^-(D^0 - \frac{\alpha Z}{|x|} + \alpha V_\gamma - g'(\rho_\gamma))\Lambda^- \\ & \leq -\left(1 - \frac{(\pi/2 + 2/\pi)\alpha N}{2}\right)|D^0|\Lambda^- \\ & < 0, \end{aligned}$$

and

$$\begin{aligned} & \Lambda^+(D^0 - \frac{\alpha Z}{|x|} - C_{ex}(N)|D^0|)\Lambda^+ \\ & \geq \left(1 - C_{ex}(N) - \frac{(\pi/2 + 2/\pi)\alpha Z}{2}\right)|D^0|\Lambda^+ \\ & > 0. \end{aligned}$$

Now we get the conclusion. □

Lemma 4.1.

$$\sigma_{\mathcal{F},ess}(Z, N) \geq 1 - C_{ex}(N).$$

Furthermore if $\mathcal{F} = H^{1/2}$,

$$\sigma_{\mathcal{F},ess}(Z, N) = 1 - C_{ex}(N).$$

Proof. Note that

$$\begin{aligned}\sigma_{\mathcal{F},k}(Z, N) &\geq \inf_{\substack{V \text{ subspace of } \Lambda^+ \mathcal{F} \\ \dim V = k}} \sup_{u \in V \setminus \{0\}} \frac{((D^0 - \frac{\alpha Z}{|x|} - C_{ex}(N)|D^0|)u, u)}{\|u\|_{L^2}^2} \\ &\geq \inf_{\substack{V \text{ subspace of } \Lambda^+ H^{1/2} \\ \dim V = k}} \sup_{u \in V \setminus \{0\}} \frac{(\Lambda^+((1 - C_{ex}(N))D^0 - \frac{\alpha Z}{|x|})\Lambda^+ u, u)}{\|u\|_{L^2}^2}.\end{aligned}$$

The operator $\Lambda^+((1 - C_{ex}(N))D^0 - \frac{\alpha Z}{|x|})\Lambda^+$ consists of an infinite number of isolated eigenvalues of finite multiplicity which accumulate at $1 - C_{ex}(N)$, see [BE11, Theorem 3.3.1]. Thus, we know that

$$\sigma_{ess}(Z, N) \geq 1 - C_{ex}(N).$$

On the other hand, we have that

$$\begin{aligned}D^0 - \frac{\alpha Z}{|x|} - C_{ex}(N)|D^0| &= (1 - C_{ex}(N))\Lambda^+|D^0|\Lambda^+ + \frac{\alpha Z}{|x|} - (1 + C_{ex}(N))\Lambda^-|D^0|\Lambda^- \\ &\leq (1 - C_{ex}(N))\Lambda^+|D^0|\Lambda^+ + \frac{\alpha Z}{|x|} - (1 - C_{ex}(N))\Lambda^-|D^0|\Lambda^- \\ &= (1 - C_{ex}(N))D^0 + \frac{\alpha Z}{|x|}.\end{aligned}$$

Thus, if $\mathcal{F} = H^{1/2}$

$$\sigma_{\mathcal{F},k}(Z, N) \leq \inf_{\substack{V \text{ subspace of } \Lambda^+ H^{1/2} \\ \dim V = k}} \sup_{u \in (V \oplus \Lambda^- H^{1/2}) \setminus \{0\}} \frac{(((1 - C_{ex}(N))D^0 - \frac{\alpha Z}{|x|})u, u)}{\|u\|_{L^2}^2}$$

The operator $(1 - C_{ex}(N))D^0 - \frac{\alpha Z}{|x|}$ consists equally of an infinite number of isolated eigenvalues of finite multiplicity accumulating at $1 - C_{ex}(N)$, see [BE11, Theorem 3.1.5]. Therefore,

$$\sigma_{ess}(Z, N) \leq 1 - C_{ex}(N).$$

It immediately yields the claimed equation. \square

5 Existence of solutions

Now, we follow the ideas of [WOL72, Lio87]. Set

$$S(N) := \{\rho \in L^1(\mathbb{R}_+); 0 \leq \rho, \int_0^\infty \rho(s) ds = N\},$$

and consider the boundary value problem:

$$D_\rho^{\text{DKS}, m_j, \kappa_j}(Z)u := (D^{0, m_j, \kappa_j} - \frac{Z}{r} + \frac{\alpha}{r} f_\rho(r) - g'_\rho(r))u = \lambda u, \quad (5.1)$$

with initial datum

$$u(0) = 0, \quad (5.2)$$

and the normalizing conditions

$$\int_0^\infty |u|^2(s) ds = 1. \quad (5.3)$$

Herein λ is the eigenvalue and $\rho \in S(N)$.

Lemma 5.1. *For any $\rho \in S(N)$ and for each positive integer $(j, m_j, \kappa_j) \in \mathcal{J}$, there are constants $0 \leq \sigma_{H_{m_j, \kappa_j, k}^{1/2}} \leq 1$ and $0 \leq \sigma_{H_{m_j, \kappa_j}^{1/2}} \leq 1$ independent of ρ such that the k -th eigenvalue $\sigma_{\rho, k}^{m_j, \kappa_j}(Z)$ of equation (5.1) satisfying (5.2) if it exists is situated in the interval $[\sigma_{H_{m_j, \kappa_j, k}^{1/2}}, \sigma_{H_{m_j, \kappa_j}^{1/2}}^k]$.*

Furthermore, for fixed $(j, m_j, \kappa_j) \in \mathcal{J}$, any eigenvalue is single. And if $\sigma_{H_{m_j, \kappa_j}^{1/2}}^k < 1 - C_{ex}(N)$, then it is the k -th eigenvalue.

Proof. It is an application of the Lemma 2.3, herein let $\mathcal{F} = H_{m_j, \kappa_j}^{1/2}$. Note that

$$\sigma_{H_{m_j, \kappa_j, k}^{1/2}}(Z, N) := \sigma_k(D^{0, m_j, \kappa_j} - \frac{\alpha Z}{|r|} - C_{ex}(N)|D^{0, m_j, \kappa_j}|),$$

and

$$\sigma_{H_{m_j, \kappa_j}^{1/2}}^k(Z, N) := \sigma^k(D^{0, m_j, \kappa_j} - \frac{\alpha(Z - N)}{|r|}).$$

Thus by Lemma 2.3 we get that

$$\sigma_{\rho, k}^{m_j, \kappa_j}(Z) = \sigma_{H_{m_j, \kappa_j, k}^{1/2}}(D_\rho^{\text{DKS}}(Z)) \geq \sigma_{H_{m_j, \kappa_j, k}^{1/2}}(Z, N)$$

and

$$\sigma_{\rho, k}^{m_j, \kappa_j}(Z) = \sigma_{H_{m_j, \kappa_j, k}^{1/2}}(D_\rho^{\text{DKS}}(Z)) \leq \sigma_{H_{m_j, \kappa_j}^{1/2}}^k(Z, N).$$

As $H_{m_j, \kappa_j}^{1/2} \subset H^{1/2}$, we know that

$$\sigma_{H_{m_j, \kappa_j, ess}^{1/2}}(Z, N) = \sigma_{ess}(D^{0, m_j, \kappa_j} - \frac{\alpha Z}{|r|} - C_{ex}(N)|D^{0, m_j, \kappa_j}|) \geq 1 - C_{ex}(N).$$

Thus, if $\sigma_{H_{m_j, \kappa_j}^{1/2}}^k(Z, N) < 1 - C_{ex}(N)$, then $\sigma_{\rho, k}^{m_j, \kappa_j}(Z)$ is an eigenvalue for the operator $D_\gamma^{\text{DKS}, m_j, \kappa_j}$.

Now, we prove the simplicity of the eigenvalues. It follows from the ODE theories that the equation 5.1 satisfying (5.2) with eigenvalue $\sigma_{\rho, k}^{m_j, \kappa_j}(Z)$ has a unique solution:

$$u_k(r) = C \exp\{-i\sigma_2 \int_0^r \left(\frac{\kappa_j}{t} \sigma_1 + \sigma_3 - \frac{Z}{t} + \frac{\alpha}{s} f(s) - g(s) - \sigma_{\rho, k}^{m_j, \kappa_j}(Z) \right) ds\}$$

where C is the normalizing constant. \square

Recall that $\sigma_{H_{m_j, \kappa_j}^{1/2}}^k(Z, N)$ defined in Lemma 2.3 is the upper bound of the k -th eigenvalue of operator operator $D_\rho^{\text{DKS}}(Z)$. Let $N^*(Z, N) = \max\{k \in \mathbb{Z}_+; \sigma_{H_{m_j, \kappa_j}^{1/2}}^k(Z, N) < 1 - C_{ex}(N)\}$. By virtue of the partial wave decomposition,

$$D_0^{\text{DKS}}(Z - N) = \bigoplus_{(j, m_j, \kappa_j) \in \mathcal{J}} D_0^{\text{DKS}, m_j, \kappa_j}(Z - N),$$

and

$$\cup_{k \in \mathbb{Z}_+} \{\sigma_{H^{1/2}}^k(Z, N)\} = \bigcup_{(j, m_j, \kappa_j) \in \mathcal{J}} \cup_{k \in \mathbb{Z}_+} \{\sigma_{H_{m_j, \kappa_j}^{1/2}}^k(Z, N)\}.$$

Thus, for any $N \leq N^*(Z, N)$ there exists a set $(k_i, j_i, m_{j_i}, \kappa_{j_i})_{1 \leq i \leq N} \subset \mathbb{Z}_+ \times \mathcal{J}$ such that for any $1 \leq i \leq N$

$$\sigma_{H_{m_{j_i}, \kappa_{j_i}}^{1/2}}^{k_i}(Z, N) \leq \sigma_{H^{1/2}}^{N^*}(Z, N) < 1 - C_{ex}(N).$$

In particular, $(k_i, j_i, m_{j_i}, \kappa_{j_i})_{1 \leq i \leq N}$ could be such that $(\sigma_{H_{m_{j_i}, \kappa_{j_i}}^{1/2}}^{k_i}(Z, N))_{1 \leq i \leq N}$ are the first N eigenvalues of the operator $D_0^{\text{DKS}}(Z - N)$.

Let $u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}$ be solution of equation (5.1) satisfying the conditions (5.2) and (5.3) with $\lambda := \sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z)$. Now, we define the operators $T(\rho)$ and $\rho_T(\rho)$ respectively by

$$T(\rho) := \sum_{i=1}^N |u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}\rangle \langle u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}|,$$

and

$$\rho_T(\rho) := \sum_{i=1}^N |u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}|^2.$$

Obviously,

$$\rho(T)(S(N)) \subset S(N).$$

As $S(N)$ is convex and closed, in order to utilise the Schauder fixed-point theory we only need the continuity and relative compactness of operator ρ_T .

Lemma 5.2. *T is continuous on $S(N)$.*

Proof. We prove first that the eigenvalues $\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z)$ are continuous in terms of ρ . For any $u \in H^{1/2}$, for $\rho_n \xrightarrow[n \rightarrow \infty]{} \rho$ in L^1 we have that

$$(|V_{\rho - \rho_n}|u, u) \leq \frac{\pi}{2} \|\rho - \rho'\|_{L^1} \| |D^0|^{1/2} u \|_{L^2} \rightarrow 0. \quad (5.4)$$

The study of the exchange-correlation functional is a bit complicated. As $\rho_n \rightarrow \rho$ in L^1 , passing to a subsequence we can also assume that $\rho_n \rightarrow \rho$ almost everywhere. By Assumption 2.1, $g' \in C^0$. Then, $g'(\rho_n) \rightarrow g'(\rho)$ almost everywhere. In addition, let $h_n(u) := C_{g,1}(\rho_n^{\beta-} + \rho_n^{\beta+})|u|^2$. Similar to the proof of inequality (3.1), as $|\rho_n^\beta - \rho^\beta| \leq |\rho_n - \rho|^\beta$ for any $0 < \beta \leq 1/3$, it is easy to see that for any $u \in H^{1/2}$, we have $h_n(u) \in L^1$ and $h_n(u) \rightarrow h(u)$ in L^1 . By virtue of Assumption 2.1, $g'(\rho_n)|u|^2 \leq h_n(u)$. Now, by the Generalized Dominated Convergence Theorem, we know that for $u \in H^{1/2}$

$$g'(\rho_n)|u|^2 \rightarrow g'(\rho)|u|^2 \quad \text{in } L^1,$$

or equivalently

$$\| |g'(\rho_n) - g'(\rho)|^{1/2} |D^0|^{-1/2} \|_{\mathcal{B}(L^2)} \rightarrow 0. \quad (5.5)$$

Now, we use the Formula (4.1) again. By virtue of the relationship of $\Lambda^+ u$ and $\Lambda^- u$, indeed the k -th eigenvalue can be reformulated by

$$\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z) = \inf_{\substack{V \text{ subspace of } \Lambda^+ H_{m_{j_i}, \kappa_{j_i}}^{1/2} \\ \dim V = k}} \sup_{u^+ \in V \setminus \{0\}} \frac{(D_\gamma^{\text{DKS}}(Z)(1 + L_\rho^{m_{j_i}, \kappa_{j_i}})u^+, (1 + L_\rho^{m_{j_i}, \kappa_{j_i}})u^+)}{\|u^+\|_{L^2}^2 + \|L_\rho^{m_{j_i}, \kappa_{j_i}} u^+\|_{L^2}^2}.$$

Herein $L_\rho^{m_j, \kappa_j}$ is the unique minimizer of the functional $\chi_- \in (\Lambda^- \mathcal{F}_{m_j, \kappa_j})^N \rightarrow (D_\rho^{\text{DKS}}(Z)(u^+ + \chi_-), (u^+ + \chi_-))$, and obviously

$$L_\rho^{m_j, \kappa_j} u^+ := U_{m_j, \kappa_j} \Lambda^- (D_\rho^{\text{DKS}}(Z))^{-1} D^0 u^+.$$

Note that by Lemma 3.2 the operator $(D_\rho^{\text{DKS}}(Z))^{-1} D^0$ is bounded in $\mathcal{B}(H^{1/2})$ and furthermore

$$\begin{aligned} & \|D_\rho^{-1}(Z)D^0 - D_{\rho_n}^{-1}(Z)D^0\|_{\mathcal{B}(H^{1/2})} \\ &= \| |D^0|^{1/2} (D_\rho^{\text{DKS}}(Z))^{-1} (\alpha V_{\rho-\rho_n} - (g'(\rho) - g'(\rho_n))) (D_{\rho_n}^{\text{DKS}}(Z))^{-1} D^0 |D^0|^{-1/2} \|_{\mathcal{B}(L^2)} \\ &\leq (1 - \kappa)^{-2} \left(\| |D^0|^{-1/2} V_{\rho-\rho_n} |D^0|^{-1/2} \|_{\mathcal{B}(L^2)} + \| |D^0|^{-1/2} |g'(\rho) - g'(\rho_n)|^{1/2} |D^0|^{-1/2} \|_{\mathcal{B}(L^2)}^2 \right) \\ &\rightarrow 0 \end{aligned}$$

Thus, the operator $L_\rho^{m_j, \kappa_j}$ is bounded in $\mathcal{B}(H_{m_j, \kappa_j}^{1/2})$ and continuous in terms of ρ . On the other hand, the operator D_ρ^{DKS} is continuous in terms of ρ . Hence we conclude that $\sigma_{\rho, k_i}^{m_j, \kappa_j}(Z)$ is continuous with respect to $\rho \in S(N)$.

By Lemma 5.1, the corresponding eigenfunction $u_{\rho, k_i}^{m_j, \kappa_j}$ to the eigenvalue $\sigma_{\rho, k_i}^{m_j, \kappa_j}(Z)$ under the conditions (5.2) and (5.3) is unique. By Cauchy's integral formula, there is a constant ϵ_i small enough satisfying

$$B(\sigma_{\rho, k_i}^{m_j, \kappa_j}(Z), \epsilon_i) \cap \sigma(D_\rho^{\text{DKS}, m_j, \kappa_j}(Z)) = \sigma_{\rho, k_i}^{m_j, \kappa_j}(Z),$$

and

$$\text{dist}(\sigma(D_\rho^{\text{DKS}, m_j, \kappa_j}(Z)), \partial B(\sigma_{\rho, k_i}^{m_j, \kappa_j}(Z), \epsilon_i)) = \epsilon_i,$$

such that $T(\rho) = \sum_{i=1}^N T_i(\rho)$ with

$$T_i(\rho) = -(2\pi i)^{-1} \int_{\partial B(\sigma_{\rho, k_i}^{m_j, \kappa_j}(Z), \epsilon_i)} (D_\rho^{\text{DKS}, m_j, \kappa_j}(Z) - z)^{-1} dz.$$

And as $\sigma_{\rho, k_i}^{m_j, \kappa_j}(Z)$ is continuous with respect to $\rho \in S(N)$, for any sequence $\rho_n \in S(N)$ such that $\rho_n \rightarrow \rho$ in L^1 , we have that for $n \geq n_0$ large enough,

$$B(\sigma_{\rho, k_i}^{m_j, \kappa_j}(Z), \epsilon_i) \cap \sigma(D_{\rho_n}^{\text{DKS}, m_j, \kappa_j}(Z)) = \sigma_{\rho_n, k_i}^{m_j, \kappa_j}(Z),$$

and

$$\text{dis}(\sigma(D_{\rho_n}^{\text{DKS}, m_j, \kappa_j}(Z)), \partial B(\sigma_{\rho, k_i}^{m_j, \kappa_j}(Z), \epsilon_i)) \geq \epsilon_i/2.$$

Consequently, we yield that $T(\rho_n) = \sum_{i=1}^N T_i(\rho_n)$ with

$$T(\rho_n) = -(2\pi i)^{-1} \sum_{i=1}^N \int_{\partial B(\sigma_{\rho_n, k_i}^{m_j, \kappa_j}(Z), \epsilon_i)} (D_{\rho_n}^{\text{DKS}, m_j, \kappa_j}(Z) - z)^{-1} dz.$$

As $\dim \text{range}(T_i) = 1$ and by Theorem A.1, we have that

$$\|\rho T(\rho) - \rho T(\rho_n)\|_{L^1} \leq \|T_\rho - T_{\rho_n}\|_{\sigma_1} \leq \sum_{i=1}^N \|T_i(\rho) - T_i(\rho_n)\|_{\mathcal{B}(L_{m_j, \kappa_j}^2)}.$$

Note that

$$\begin{aligned}
& \|T_i(\rho) - T_i(\rho_n)\|_{\mathcal{B}(L^2_{m_{j_i}, \kappa_{j_i}})} \\
& \leq \frac{1}{2\pi} \int_{\partial B(\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z), \epsilon_i)} dz \|(D_{\rho_n}^{\text{DKS}}(Z) - z)^{-1} V_{\rho - \rho} (D_{\rho}^{\text{DKS}}(Z) - z)^{-1}\|_{\mathcal{B}(L^2_{m_{j_i}, \kappa_{j_i}})} \\
& + \frac{1}{2\pi} \int_{\partial B(\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z), \epsilon_i)} dz \|(D_{\rho_n}^{\text{DKS}}(Z) - z)^{-1} (g'(\rho) - g'(\rho_n)) (D_{\rho}^{\text{DKS}}(Z) - z)^{-1}\|_{\mathcal{B}(L^2_{m_{j_i}, \kappa_{j_i}})}.
\end{aligned}$$

By Lemma 3.2, for the first term on the right hand side and for $z \in \partial B(\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z), \epsilon_i)$, we have that

$$\begin{aligned}
& \|(D_{\rho_n}^{\text{DKS}}(Z) - z)^{-1} V_{\rho - \rho} (D_{\rho}^{\text{DKS}}(Z) - z)^{-1}\|_{\mathcal{B}(L^2_{m_{j_i}, \kappa_{j_i}})} \\
& \leq \frac{\pi}{2} \|\rho_n - \rho\|_{L^1} (\|(D_{\rho_n}^{\text{DKS}}(Z) - z)^{-1} |D^0|^{1/2}\|_{\mathcal{B}(L^2)} \|(D_{\rho}^{\text{DKS}}(Z) - z)^{-1} |D^0|^{1/2}\|_{\mathcal{B}(L^2)}) \\
& \leq (1 - \kappa)^{-1} \frac{\pi}{2} \|\rho_n - \rho\|_{L^1} \|(D_{\rho_n}^{\text{DKS}}(Z) - z)^{-1} |D_{\rho_n}^{\text{DKS}}(Z)|^{1/2}\|_{\mathcal{B}(L^2)} \\
& \quad \times \|(D_{\rho}^{\text{DKS}}(Z) - z)^{-1} |D_{\rho}^{\text{DKS}}(Z)|^{1/2}\|_{\mathcal{B}(L^2)} \\
& \leq (1 - \kappa)^{-1} \frac{\pi}{2} \|\rho_n - \rho\|_{L^1} (\epsilon_i^{-1/2} + \epsilon_i^{-1}|z|) (\sqrt{2}\epsilon_i^{-1/2} + \epsilon_i^{-1}2|z|) \\
& \leq C \|\rho_n - \rho\|_{L^1}.
\end{aligned} \tag{5.6}$$

Analogously, for the second term on the right hand side and $z \in \partial B(\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z), \epsilon_i)$

$$\begin{aligned}
& \|(D_{\rho_n}^{\text{DKS}}(Z) - z)^{-1} (g'(\rho) - g'(\rho_n)) (D_{\rho}^{\text{DKS}}(Z) - z)^{-1}\|_{\mathcal{B}(L^2_{m_{j_i}, \kappa_{j_i}})} \\
& \leq C \| |g'(\rho) - g'(\rho_n)|^{1/2} |D^0|^{-1/2} \|_{\mathcal{B}(L^2)}^2.
\end{aligned} \tag{5.7}$$

Given that

$$|\partial B(\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z), \epsilon_i)| < \infty,$$

by Equation (5.4) and (5.5) for any $\rho_n \rightarrow \rho$ in L^1 we have that

$$\|T_i(\rho) - T_i(\rho_n)\|_{\mathcal{B}(L^2_{m_{j_i}, \kappa_{j_i}})} \rightarrow 0.$$

Now, T is continuous on $S(N)$. This ends the proof. \square

Lemma 5.3. T is compact on $S(N)$.

Proof. It is sufficient to prove that $T(\rho_n)$ is relatively compact in $S(N)$. As $N \leq N^*(Z, N)$, we have that for $1 \leq i \leq N$

$$\sigma_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}}(Z) \leq \sigma_{H^{1/2}}^{N^*}(Z, N) < 1 - C_{ex}(N).$$

and

$$\|u_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}}\|_{H_{m_{j_i}, \kappa_{j_i}}^{1/2}} \leq C.$$

Up to a subsequence, we have that for $1 \leq i \leq N$

$$\sigma_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}}(Z) \rightarrow \sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z) \in [0, 1 - C_{ex}(N))$$

and

$$u_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}} \rightharpoonup u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}} \quad \text{in } H_{m_{j_i}, \kappa_{j_i}}^{1/2}.$$

This implies that $u_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}} \rightarrow u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}$ in L_{loc}^2 .

We pick a smooth cut-off function $0 \leq \chi(|x|) \leq 1$ which equals 1 on the ball $B(0, 1)$ and 0 outside the ball $B(0, 2)$. Let $u_{n, R, i}^{(1)} := \chi(|x|/R) u_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}}$ and $u_{n, R, i}^{(2)} := (1 - \chi(|x|/(4R))) u_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}}$, and $u_{n, R, i}^{(3)} := (\chi(|x|/(4R)) - \chi(|x|/R)) u_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}}$. Obviously, we have that

$$u_{n, R, i}^{(1)} \rightarrow u_{*, R, i}^{(1)} := (1 - \chi(|x|/R)) u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}} \quad \text{in } L^2,$$

and

$$u_{n, R, i}^{(3)} \rightarrow u_{*, R, i}^{(3)} := (\chi(|x|/(4R)) - \chi(|x|/R)) u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}} \quad \text{in } L^2.$$

Thus, we have that

$$(D_{\rho_n}^{\text{DKS}, m_{j_i}, \kappa_{j_i}}(Z) - \sigma_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}}(Z))(u_{n, R, i}^{(1)} + u_{n, R, i}^{(2)}) = f_{n, R, i}$$

with $f_{n, R, i} := (D_{\rho_n}^{\text{DKS}, m_{j_i}, \kappa_{j_i}}(Z) - \sigma_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}}(Z)) u_{n, R, i}^{(3)}$. By virtue of the fact that $\text{supp } u_{n_1, i}^{(1)}$ and $\text{supp } u_{n_1, i}^{(2)}$ are disjoint,

$$\|u_{n, R, i}^{(2)}\|_{L_{m_{j_i}, \kappa_{j_i}}^2} \leq \|(D_{\rho_n}^{\text{DKS}, m_{j_i}, \kappa_{j_i}}(0) - \sigma_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}}(Z))^{-1} (Zr^{-1} u_{n, R, i}^{(2)} + f_{n, R, i})\|_{L_{m_{j_i}, \kappa_{j_i}}^2}.$$

According to Lemma 2.3, Lemma 4.1 and Lemma 5.1, $\sigma(D_{\rho_n}^{\text{DKS}, m_{j_i}, \kappa_{j_i}}(0)) \cap \mathbb{R}_+ \subset [1 - C_{ex}(N), \infty)$ for any $\gamma_n \in \Gamma_N$. This and the fact $\sigma_{\rho_{n_l}, k_i}^{m_{j_i}, \kappa_{j_i}}(Z) \sigma_{\rho_*, k_i}^{m_{j_i}, \kappa_{j_i}}(Z) < 1 - C_{ex}(N)$ imply that the operators $(D_{\rho_n}^{\text{DKS}, m_{j_i}, \kappa_{j_i}}(0) - \sigma_{\rho_{n_l}, k_i}^{m_{j_i}, \kappa_{j_i}}(Z))^{-1}$ are uniformly bounded. Hence,

$$\|u_{n, R, i}^{(2)}\|_{L_{m_{j_i}, \kappa_{j_i}}^2} \leq \|u_{n, R, i}^{(3)}\|_{L_{m_{j_i}, \kappa_{j_i}}^2} + \frac{Z}{R} \|u_{n, R, i}^{(2)}\|_{L_{m_{j_i}, \kappa_{j_i}}^2} + \frac{Z}{4R} \|u_{n, R, i}^{(2)}\|_{L_{m_{j_i}, \kappa_{j_i}}^2}$$

As a result,

$$\begin{aligned} & \|u_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}} - u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}\|_{L_{m_{j_i}, \kappa_{j_i}}^2} \\ & \leq \|u_{n, R, i}^{(2)}\|_{L_{m_{j_i}, \kappa_{j_i}}^2} + \|u_{n, R, i}^{(3)}\|_{L_{m_{j_i}, \kappa_{j_i}}^2} + \|u_{n, R, i}^{(1)} - u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}\|_{L_{m_{j_i}, \kappa_{j_i}}^2} \\ & \leq 2\|u_{n, R, i}^{(3)}\|_{L_{m_{j_i}, \kappa_{j_i}}^2} + \|u_{n, R, i}^{(1)} - u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}\|_{L_{m_{j_i}, \kappa_{j_i}}^2} + \frac{C}{R} \\ & \xrightarrow{n \rightarrow \infty} 2\|u_{*, R, i}^{(3)}\|_{L_{m_{j_i}, \kappa_{j_i}}^2} + \|(1 - \chi(|x|/R)) u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}\|_{L_{m_{j_i}, \kappa_{j_i}}^2} + \frac{C}{R} \\ & \xrightarrow{R \rightarrow \infty} 0. \end{aligned}$$

Thus, T is compact. \square

Now, under the assumption $N \leq N^*(Z, N) = \max\{k \in \mathbb{Z}_+; \sigma_{H^{1/2}}^k(Z, N) < 1 - C_{ex}(N)\}$, there exists a solution set $(u_{k_i, m_{j_i}, \kappa_{j_i}}, \lambda_{k_i, m_{j_i}, \kappa_{j_i}})_{1 \leq i \leq N}$ of equations 2.3 under the conditions (2.5) and (2.4). By Lemma 5.1, for any $1 \leq i \leq N$

$$\sigma_{H_{m_{j_i}, \kappa_{j_i}}^{1/2}, k_i}^{k_i}(Z, N) \leq \lambda_{k_i, m_{j_i}, \kappa_{j_i}} \leq \sigma_{H_{m_{j_i}, \kappa_{j_i}}^{1/2}}^{k_i}(Z, N).$$

In particular, $(k_i, j_i, m_{j_i}, \kappa_{j_i})_{1 \leq i \leq N}$ could be such that $(\sigma_{H_{m_{j_i}, \kappa_{j_i}}^{1/2}}^{k_i}(Z, N))_{1 \leq i \leq N}$ are the first N eigenvalues of the operator $D_0^{\text{DKS}}(Z - N)$. Thus,

$$\sigma_{H^{1/2}, i}(Z, N) \leq \lambda_{k_i, m_{j_i}, \kappa_{j_i}} \leq \sigma_{H^{1/2}}^i(Z, N).$$

And now, we consider the assumption $N \leq N^*(Z, N)$ with $\sigma_{H^{1/2}}^{N^*}(Z, N) = 1 - C_{ex}(N)$. We follow the idea of the proof of Theorem III.3 in [Lio87]. In this case, we approximate Z by $Z + \epsilon$. Thus, we have that $N \leq N^*(Z + \epsilon, N) = \max\{k \in \mathbb{Z}_+; \sigma_{H^{1/2}}^k(Z + \epsilon, N) < 1 - C_{ex}(N)\}$. Let $(u_1^\epsilon, \lambda_1^\epsilon, \dots, u_N^\epsilon, \lambda_N^\epsilon)$ be the solution set. Then we have that $u_i^\epsilon \xrightarrow{*} u_i$ in $H^{1/2}$. If $\sum \|u_i\|_{L^2}^2 := N' < N$, then the limit operator has at least N eigenvalues since $\sigma_{H^{1/2}}^k(Z, N') < \sigma_{H^{1/2}}^k(Z, N) \leq 1 - C_{ex}(N)$. In particular, $\lambda_i^\epsilon \rightarrow \lambda_i < 1 - C_{ex}(N)$. By virtue of Lemma 5.3 we deduce the strong convergence of u_i^ϵ to u_i in L^2 reaching a contradiction. Therefore, $u_i^\epsilon \rightarrow u_i$ strongly in L^2 . This ends the proof of Theorem 2.5.

6 Existence of minimizers

6.1 Existence of minimizers for $N < Z$

From now on, we can prove the existence of minimizers. The following theorem is inspired by the work [HS07]:

Theorem 6.1. *Under the Assumption 2.2 and with the same assumption as in Theorem 2.6 for $N < Z$, there is a constant $\nu < \sigma_{H^{1/2}, ess}(Z, N)$, such that*

$$E^{\text{DKS}}(Z, N) = \inf\{\mathcal{E}^{\text{DKS}}(Z)(\gamma), \gamma \in \Gamma_{\text{ps}, Z, N, \nu}^+\}$$

with

$$\Gamma_{\text{ps}, Z, N, \nu}^+ := \{\gamma \in \Gamma_{\text{ps}, Z, N}^+; \gamma = \sum_{k=1}^N |u_k\rangle \langle u_k|, D_\rho^{\text{DKS}}(Z)u_k = \nu_k u_k \text{ with } 0 < \nu_1 \leq \dots \leq \nu_N < \nu\}.$$

Proof. Under the assumption, obviously there is a constant $\nu < \sigma_{H^{1/2}, ess}(Z, N)$, such that

$$E^{\text{DKS}}(Z, N) < (1 - \tau) \left(\sum_{k=1}^{N-1} \sigma_k(Z, N) + \nu \right).$$

By Lemma 3.1, there are several eigenfunctions for the operator $D_{\rho\gamma}^{\text{DKS}}(Z)$ if $N < Z$. Thus the contradiction can be constructed. We assume otherwise that $\gamma' = \sum_{k=1}^N |u_k\rangle \langle u_k|$ minimizes $\mathcal{E}^{\text{DKS}}(Z)(\gamma)$ in $\Gamma_{\text{ps}, Z, N}^+$ and there is a constant $1 \leq l \leq N$, such that for $k \geq l$, $D_\rho^{\text{DKS}}(Z)u_l = \nu_l u_l$ with $\nu \leq \nu_k$.

Now, by Lemma 3.1, we know that

$$\begin{aligned} \mathcal{E}^{\text{DKS}}(Z)(\gamma') &\geq (1 - \tau) \text{Tr}_{L^2} D_{\rho\gamma'}^{\text{DKS}}(Z, N)\gamma' \\ &= (1 - \tau) \sum_{k=1}^{l-1} \nu_k + (1 - \tau) \sum_{k=l}^N \nu_k. \end{aligned}$$

By Lemma 2.3 again, we know that

$$\nu_k \geq \sigma_{H^{1/2}, k}(Z, N).$$

Hence,

$$\mathcal{E}^{\text{DKS}}(Z)(\gamma') \geq (1 - \tau) \left(\sum_{k=1}^{N-1} \sigma_{H^{1/2}, k}(Z, N) + \nu \right) > E^{\text{DKS}}(Z, N).$$

This is a contradiction. Thus we get the conclusion. \square

For any minimizing sequence $\gamma_n := \sum_{k=1}^N |u_{n,k}\rangle \langle u_{n,k}| \in \Gamma_{\text{ps},Z,N,\nu}^+$, we have that

$$D_{\rho_{\gamma_n}}^{\text{DKS}}(Z)u_{n,k} = \nu_{n,k}u_{n,k}.$$

By Lemma 2.3, we know that $(u_{n,k})_{n \geq 1}$ is uniformly bounded in $H^{1/2}$ from above, and $h_0 \leq \nu_{n,k} < \nu$. Thus, we have that up to a subsequence, there is a $\gamma_* := \sum_{k=1}^N |u_k\rangle \langle u_k|$ such that

$$(\nu_{n,k})_{1 \leq k \leq N} \xrightarrow{n \rightarrow \infty} (\nu_k)_{1 \leq k \leq N} \in [h_0, \nu],$$

and

$$\nu_k \leq \nu_l \quad \text{if } k \leq l,$$

and

$$(u_{n,k})_{1 \leq k \leq N} \xrightarrow{n \rightarrow \infty} (u_k)_{1 \leq k \leq N} \quad \text{in } H^{1/2}, \quad (6.1)$$

as well as

$$(u_{n,k})_{1 \leq k \leq N} \xrightarrow{n \rightarrow \infty} (u_k)_{1 \leq k \leq N} \quad \text{in } L_{\text{loc}}^2. \quad (6.2)$$

Lemma 6.2. *For all $1 \leq k \leq N$, up to a subsequence $u_{n,k} \rightarrow u_k$ strongly in $H^{1/2}$.*

Proof. Arguing as in the proof of Lemma 5.3, we know that up to a subsequence

$$\|u_{n,k} - u_k\|_{L^2} \rightarrow 0,$$

thus

$$\|\rho_{\gamma_n} - \rho_{\gamma_*}\|_{L^1} \rightarrow 0.$$

Now, we are going to prove that $u_{n,k} \rightarrow u_k$ in $H^{1/2}$. Indeed, we have that

$$\begin{aligned} \|u_{n,k} - u_k\|_{H^{1/2}} &= \|\nu_{n,k}(D_{\rho_{\gamma_n}}^{\text{DKS}}(Z))^{-1}u_{n,k} - \nu_k(D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1}u_k\|_{H^{1/2}} \\ &\leq o(1) + \nu_k \|((D_{\rho_{\gamma_n}}^{\text{DKS}}(Z))^{-1} - (D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1})u_{n,k}\|_{H^{1/2}} \\ &\quad + \nu_k \|(D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1}(u_{n,k} - u_k)\|_{H^{1/2}} \\ &\leq o(1) + \nu_k \|(D_{\rho_{\gamma_n}}^{\text{DKS}}(Z))^{-1}V_{\rho_{\gamma_n} - \rho_{\gamma_*}}(D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1}u_{n,k}\|_{H^{1/2}} \\ &\quad + \nu_k \|(D_{\rho_{\gamma_n}}^{\text{DKS}}(Z))^{-1}(g'(\rho_{\gamma_n}) - g'(\rho_{\gamma_*}))(D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1}u_{n,k}\|_{H^{1/2}}. \end{aligned}$$

Similar to the estimates (5.6) and (5.7), we have that

$$\begin{aligned} &\| |D^0|^{1/2}(D_{\rho_{\gamma_n}}^{\text{DKS}}(Z))^{-1}V_{\rho_{\gamma_n} - \rho_{\gamma_*}}(D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1}u_{n,k}\|_{L^2} \\ &\leq \frac{\pi}{2} \|\rho_{\gamma_n} - \rho_{\gamma_*}\|_{L^1} \| |D^0|^{1/2}(D_{\rho_{\gamma_n}}^{\text{DKS}}(Z))^{-1}|D^0|^{1/2}\|_{\mathcal{B}(L^2)} \| |D^0|^{1/2}(D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1}u_{n,k}\|_{L^2} \\ &\leq (1 - \kappa)^{-2} \frac{\pi}{2} \|\rho_{\gamma_n} - \rho_{\gamma_*}\|_{L^1} \| |D^0|^{-1/2}u_{n,k}\|_{L^2}. \end{aligned}$$

Analogously,

$$\begin{aligned} &\| (D_{\rho_{\gamma_n}}^{\text{DKS}}(Z))^{-1}(g'(\rho_{\gamma_*}) - g'(\rho_{\gamma_n}))(D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1}u_{n,k}\|_{L^2} \\ &\leq (1 - \kappa)^{-2} \| |g'(\rho_{\gamma_*}) - g'(\rho_{\gamma_n})|^{1/2}|D^0|^{-1/2}\|_{\mathcal{B}(L^2)} \| |D^0|^{-1/2}u_{n,k}\|_{L^2}. \end{aligned}$$

Consequently, by equations (5.4) and (5.5), we know that

$$\|u_{n,k} - u_k\|_{H^{1/2}} \rightarrow 0.$$

□

Now, we have proved that $\gamma_* \in \Gamma_{\text{ps}, Z, N}^+$. The existence of minimizers will be proved if we show that

$$E_{\text{ex}}(\rho_{\gamma_n}) \rightarrow E_{\text{ex}}(\rho_{\gamma_*}).$$

Given that

$$\|\rho_{\gamma_*} + t(\rho_{\gamma_n} - \rho_{\gamma_*})\|_{L^1} \leq (1-t)\|\rho_{\gamma_*}\|_{L^1} + t\|\rho_{\gamma_n}\|_{L^1} = N,$$

using again the Equation (3.1), we yield that

$$\begin{aligned} |E_{\text{ex}}(\rho_{\gamma_n}) - E_{\text{ex}}(\rho_{\gamma_*})| &= \left| \int_0^1 (g'(\rho_{\gamma_*} + t(\rho_{\gamma_n} - \rho_{\gamma_*})), \rho_{\gamma_n} - \rho_{\gamma_*}) dt \right| \\ &\leq \sum_{k=1}^N \sup_{t \in [0,1]} (|g'(\rho_{\gamma_*} + t(\rho_{\gamma_n} - \rho_{\gamma_*}))| |u_{n,k} - u_k|, |u_{n,k} + u_k|) \\ &\leq C_{\text{ex}}(N) \sum_{k=1}^N \| |D^0|^{1/2}(u_{n,k} - u_k) \|_{L^2} \| |D^0|^{1/2}(u_{n,k} + u_k) \|_{L^2} \\ &\rightarrow 0. \end{aligned}$$

Finally, we proved that

$$\mathcal{E}^{\text{DKS}}(Z)(\gamma_*) = \lim_{n \rightarrow \infty} \mathcal{E}^{\text{DKS}}(Z)(\gamma_n) =: E^{\text{DKS}}(Z, N).$$

Now, we get the conclusion.

6.2 Existence of minimizers for $Z = N$

Let $E := \max_{Z \in [N, N+\epsilon]} E(Z, N)$. By the assumption on Theorem 2.6 for $Z = N$, we know that there is a constant $\delta > 0$, such that

$$E + \delta < (1-\tau) \left(\sum_{k=1}^{N-1} \sigma_{H^{1/2}, k}(N, N) + \sigma_{H^{1/2}, \text{ess}}(N, N) \right)$$

By Lemma 2.3 and lemma 4.1, we know that $\sigma_{H^{1/2}, k}(Z, N), \sigma_{H^{1/2}, \text{ess}}(Z, N)$ are continuous and non-increasing with respect to Z . Thus, there is a constant $0 < \epsilon' < \epsilon$, such that for any $Z \in [N, N + \epsilon']$,

$$(1-\tau) \left(\sum_{k=1}^{N-1} \sigma_{H^{1/2}, k}(N, N) + \sigma_{H^{1/2}, \text{ess}}(N, N) \right) - \delta/2 \leq (1-\tau) \left(\sum_{k=1}^{N-1} \sigma_{H^{1/2}, k}(Z, N) + \sigma_{H^{1/2}, \text{ess}}(Z, N) \right).$$

Now, we have that for any $Z \in [N, N + \epsilon']$

$$E(Z, N) < (1-\tau) \left(\sum_{k=1}^{N-1} \sigma_{H^{1/2}, k}(Z, N) + \sigma_{H^{1/2}, \text{ess}}(Z, N) \right) + \delta/2.$$

And $\sigma_{H^{1/2}, \text{ess}}(Z, N)$ is independent of Z , thus there is a constant $\nu < \sigma_{H^{1/2}, \text{ess}}(Z, N)$, such that for $Z \in [N, N + \epsilon']$,

$$E(Z, N) < (1-\tau) \left(\sum_{k=1}^{N-1} \sigma_{H^{1/2}, k}(Z, N) + \nu \right).$$

By Theorem 6.1, for $Z \in (N, N + \epsilon]$

$$E^{\text{DKS}}(Z, N) = \inf\{\mathcal{E}^{\text{DKS}}(Z)(\gamma), \gamma \in \Gamma_{\text{ps}, Z, N, \nu}^+\}.$$

Now, the minimizers $\gamma_{Z,*} := \sum_{k=1}^N |u_{Z,k}\rangle \langle u_{Z,k}|$ of $E^{\text{DKS}}(Z, N)$ constructs a minimizing sequence for $E^{\text{DKS}}(Z, N)$, and $\gamma_{Z,*} \in \Gamma_{\text{ps}, Z, N, \nu}^+$. As $\nu < \sigma_{H^{1/2}, \text{ess}}(Z, N)$, repeating the proof of existence of minimizers for the case $Z > N$, we get the claimed results in Theorem 2.6.

A Inequality

We are going to prove the following inequality:

Theorem A.1.

$$\|\rho_{\gamma_1} - \rho_{\gamma_2}\|_{L^1} \leq \|\gamma_1 - \gamma_2\|_{\sigma_1}.$$

Proof. Let $h = \gamma_1 - \gamma_2$, then

$$\rho_h(x) = h(x, x) = \gamma_1(x, x) - \gamma_2(x, x) = \rho_{\gamma_1}(x) - \rho_{\gamma_2}(x).$$

Thus, we only need to consider the problem

$$\|\rho_h\|_{L^1} \leq \text{Tr } |h|.$$

As $\gamma_1, \gamma_2 \in X$ is self-adjoint, thus h is self-adjoint, with $-\mathbb{1}_{L^2} \leq h \leq \mathbb{1}_{L^2}$. Now, we have a complete set of eigenfunctions $(u_n)_{n \geq 1}$ of h in L^2 corresponding to a sequence of eigenvalues λ_n with $|\lambda_n|$ non-decreasing, such that

$$h = \sum_{n=1}^{\infty} \lambda_n |u_n\rangle \langle u_n|.$$

Thus, we have that

$$\|\rho_h\|_{L^1} = \int \left| \sum_{n=1}^{\infty} \lambda_n |u_n|^2(x) \right| dx \leq \sum_{n=1}^{\infty} |\lambda_n| = \text{Tr}_{L^2} |h|.$$

□

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