



**HAL**  
open science

# Existence of minimisers for Dirac-Konh-Sham models in quantum chemistry

Long Meng

► **To cite this version:**

Long Meng. Existence of minimisers for Dirac-Konh-Sham models in quantum chemistry. 2021. hal-03090701v2

**HAL Id: hal-03090701**

**<https://hal.science/hal-03090701v2>**

Preprint submitted on 24 Mar 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# 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. Then we can redefine the ground state: instead of defining it on the whole space  $H^{1/2}$  by the critical point theory, we define it on the set of the solutions. Based on an energy criteria, we can prove the existence of minimizers.

## 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

---

\*LONG MENG, DIPARTIMENTO DI MATEMATICA, UNIVERSITÀ DEGLI STUDI DI PADOVA *E-mail address:* [meng@math.unipd.it](mailto:meng@math.unipd.it)

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. The ground energy and ground state can thus be defined on the positive spectral subspaces of the corresponding Dirac-Fock operator [ES01, ES02]. Based on this definition of the ground state, some retraction methods and fixed point theories have been introduced to handle with the problem of Dirac-Fock model, see [HS07, Sér21]. Furthermore, the retraction methods in [Sér21] can be utilized to deal with the Dirac-Fock models for crystals [CMPS21] which is more delicate due to the compactness issues.

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

Nevertheless, following the idea of [WOL72, Lio87], on account of the spherical symmetry we can prove the existence of solutions of Dirac-Kohn-Sham equations by using the Schauder's fixed-point theorem. Furthermore, our result shows that the non-relativistic LDA type exchange functional can be reached.

As mentioned above, we can not use the critical point theory to prove the ground state. Now, we use the second definition. For the standard DFT theory with integer occupation number, the minimizer is indeed one of the solutions of the Dirac-Kohn-Sham equations. Thus we redefine the ground state of the Dirac-Kohn-Sham model on the set of solutions which is non empty under the spherical symmetry condition. Inspired by the work [HS07] and the binding condition of the models in quantum chemistry (see for example [HLS09]), we proposed a stronger energy criteria for the Dirac-Kohn-Sham model under which any minimizing sequence is precompact in  $H^{1/2}$ . It is showed that the when the non relativistic LDA type exchange functional is small enough, we can calculate at least one electrons for some proper nuclear charges.

## 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  $\Lambda^+$  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

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

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  $\gamma$  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  $\gamma$  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  $\gamma$  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,  $V_{\rho_\gamma}$  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  $\alpha$  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 the critical point theory [ES99, Lev14], via the fixed point theory [HS07], or via a retraction technique [Sér21, CMPS21]. 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

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

Here  $h(\Psi^+)$  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  $\mathcal{E}^{\text{DF}}$  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  $D_\gamma^{\text{DF}}$  [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  $\alpha$  is small enough and  $\alpha Z$  fixed, 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. However, they only considered the closed shell case.

Recently in [Sér21], 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 simple assumptions, 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 at most of class  $C^{1,1/3}$ , 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  $\gamma_*$  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  $\Gamma_N^+$ :

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

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

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

*Remark 2.1.* In rDFT, sometimes the ground state is defined on the set

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

But under our assumptions in Section 2.4, indeed  $\Gamma_{\text{ps},Z,N}^+$  and  $\tilde{\Gamma}$  are equivalent since there are no eigenvalues in  $(-1, 0]$  according to Lemma 2.4 which will be mentioned below.

### 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. Even though it is hopeless for the author to use critical point theory to prove the existence of solutions, inspired by the work [WOL72, Lio87] we can still prove the existence of solutions in the spherical symmetric situation.

Before going further, we introduce the partial wave decomposition and its 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  $\Phi_{m_j, \kappa_j}^+$  and  $\Phi_{m_j, \kappa_j}^-$ . 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  $L_{m_j, \kappa_j}$  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  $\gamma$  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

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

And we will study the existence of solutions of the Dirac-Kohn-Sham equation in  $L^2(\mathbb{R}_+) \otimes \mathfrak{H}_{m_j,\kappa_j}$  in Section 5, 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

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

must be satisfied.

Additional functional space related to the partial wave decomposition 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

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

with the norm

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

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

$$g(0) = 0, \quad (2.5a)$$

$$g' \leq 0, \quad (2.5b)$$

$$\exists 0 < \beta_- \leq \beta_+ \leq \frac{1}{3} \quad \text{s.t.} \quad \sup_{\rho \in \mathbb{R}_+} \frac{|g'(\rho)|}{\rho^{\beta_-} + \rho^{\beta_+}} \leq C_{g,1}, \quad (2.5c)$$

$$\text{and} \quad \sup_{\rho \in \mathbb{R}_+} \frac{|g(\rho) - \rho g'(\rho)|}{\rho^{1+\beta_-} + \rho^{1+\beta_+}} \leq C_{g,2}, \quad (2.5d)$$

$$|g'(\rho) - g'(\rho')| \leq C_{g,3} |g'(|\rho - \rho'|)| \quad (2.5e)$$

*Assumption 2.3.* Let

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

be the sharp constant for the corresponding Sobolev inequality. And let  $C_{ex}(N) := C_{g,1} \left( N^{\beta_+} C_{\text{sob},\beta_+}^2 + N^{\beta_-} C_{\text{sob},\beta_-}^2 \right)$ . We assume that

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

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

**Lemma 2.4.** *Under the Assumption 2.2 and 2.3, and assume that  $0 \leq \rho$ ,  $\|\rho\|_{L^1} = N$ ,  $N < Z$  and  $\mathcal{F}$  is a subspace of  $H^{1/2}$  such that  $\mathcal{F} = \Lambda^+ \mathcal{F} \oplus \Lambda^- \mathcal{F}$ . Then*

- (Negative eigenvalues) *There is no eigenvalues in  $(-1, 0]$ .*
- (Positive eigenvalues) *There are constants  $0 < \sigma_{\mathcal{F},k}(Z, N) \leq 1$  and  $0 < \sigma_{\mathcal{F}}^k(Z, N) \leq 1$  independent of  $\rho$  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  $k$ .*

- (Positive essential spectrum) *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 positive essential spectrum on the subspace  $\mathcal{F}$ . Then  $b \in [\sigma_{\mathcal{F},\text{ess}}(Z, N), \sigma_{\mathcal{F}}^{\text{ess}}(Z, N)]$ .*

*Furthermore, for any  $\nu < \sigma_{\mathcal{F},\text{ess}}(Z, N)$ , there is a constant  $M \in \mathbb{Z}_+$ , such that there are at most  $M$  eigenvalues in the interval  $[0, \nu]$ .*

The proof is situated in Section 4.

Unlike the Dirac-Fock model, we can not guarantee the existence of the  $N$ -th eigenvalue in the interval  $(0, \sigma_{H^{1/2},\text{ess}}](Z, N)$  according to Lemma 2.4 if the bottom of the positive essential spectrum  $b > \sigma_{H^{1/2},\text{ess}}$ . And by Lemma 4.1,  $\sigma_{H^{1/2},\text{ess}} = 1 - C_{ex}(N)$ . Thus for the existence of solutions, we need the following assumption:

*Assumption 2.5.* Let  $N^*(Z, N) = \max\{k \in \mathbb{Z}_+; \sigma_{H^{1/2}}^k(Z, N) \leq 1 - C_{ex}(N)\}$ . We assume  $N \leq N^*(Z, N)$ .

Now, we obtained the following theorem about the existence of solutions under the spherical symmetric condition:

**Theorem 2.6.** *Under Assumptions 2.2, 2.3 and 2.5, 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 (2.4). In addition, for any  $1 \leq i \leq N$*

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

*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 the operator  $D_\rho^{\text{DKS}}(Z)$  on the space  $H^{1/2}$ , and for any  $1 \leq i \leq N$*

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

The proof is situated in Section 5

*Remark 2.7.* The Assumption 2.5 implies  $N \leq Z$  by the definition of  $\sigma_{H^{1/2}}^k(Z, N)$  in the proof of Lemma 3.2.

We proved that under the spherical symmetry condition the set  $\Gamma_{\text{ps}, Z, N}^+$  is non-empty. Now, we consider the existence of minimizer.

**Theorem 2.8.** *Under the Assumption 2.2 and Assumption 2.3, if  $\Gamma_{\text{ps}, Z, N}^+ \neq \emptyset$  and under the following energy criteria*

$$E^{\text{DKS}}(Z, N) < (1 - \tau) \left( \sum_{k=1}^{N-1} \sigma_{H^{1/2}, k}(Z, N) + \sigma_{H^{1/2}, \text{ess}}(Z, N) \right), \quad (2.6)$$

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

The proof is situated in Section 6.

*Remark 2.9.* Even though in this paper we only considered the spherical symmetric situation, the Theorem 2.8 still works for the non spherical symmetric cases. And the external potential of the atom  $V = \frac{Z}{|x|}$  can be replaced by the one of the molecules.

*Remark 2.10.* The conditions (2.5a)-(2.5e) are obviously fulfilled by the non-relativistic LDA type exchange functional, namely  $g(\rho) = -\alpha C_g \rho^{4/3}$  for some constant  $C_g$ . This exchange functional is critical because of the Sobolev inequality. And in this case, indeed our problem is a critical Dirac equation for orthonormal functions.

*Remark 2.11.* If we do not consider the exchange-correlation energy (i.e.  $E_{xc}(\rho) = 0$ ), we will get the reduced Dirac-Fock model. In this case, the energy inequality 2.6 can be satisfied for  $N = 1$  and  $26 \leq Z \leq 81$ . The proof is detailed in Appendix B. Thus with the non-relativistic LDA exchange energy, the inequality 2.6 will still hold for  $N = 1$  and some proper nuclear charges  $Z$  if  $C_g$  is small enough.

*Remark 2.12.* The similar energy criteria can be used to prove the existence of minimizers for the Dirac-Fock models. And for the Dirac-Fock model, the corresponding criteria energy inequality (2.6) still holds for  $N = 1$  and some proper nuclear charges  $Z$ .

### 3 Preliminaries

In this section, we will provide some useful estimates about 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  $\gamma \in \Gamma_N$ ,

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

where

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

*Proof.* The first inequality is just the Kato inequality. And for the second one, as  $0 < \beta_- \leq \beta_+ \leq \frac{1}{3}$ , we yield

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

□

Now,

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

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

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

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

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

2. For  $\gamma \in \Gamma_{Z,N}^+$ , if  $\frac{\pi\alpha}{2} (Z + N) + C_{ex}(N) < 1$  we have

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

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

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

and

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

Thus,

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

and

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

Now for the estimates of the energy, note

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

By Assumption 2.2 and Gagliardo–Nirenberg interpolation inequality, we know

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

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

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

As

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

we have

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

Letting

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

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

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

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

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

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 2.4.* The proof is based on the min-max principle in [DES00, Theorem 1.1]. By Lemma 3.2, we know that  $\inf |\sigma(D_\rho)| > 0$ , thus 0 is not the eigenvalue.

For any  $V \subset \Lambda^+ \mathcal{F}$ , we have  $V \oplus \Lambda^- \mathcal{F} \subset \Lambda^+ \mathcal{F} \oplus \Lambda^- \mathcal{F} = \mathcal{F}$ . Thus the definition of the  $k$ -th positive eigenvalue if it exists can be formulated by

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

and the  $k'$ -th negative eigenvalue can be written as

$$\sigma'_{\mathcal{F},k'}(D_\rho^{\text{DKS}}(Z)) = \sup_{\substack{V \text{ subspace of } \Lambda^- \mathcal{F} \\ \dim V = k'}} \inf_{u \in (V \oplus \Lambda^+ \mathcal{F}) \setminus \{0\}} \frac{(D_\rho^{\text{DKS}}(Z)u, u)}{\|u\|_{L^2}^2}. \quad (4.2)$$

First we will check the assumptions for the min-max principle in [DES00]. Obviously,

$$\sigma_{\mathcal{F},1}(D_\rho^{\text{DKS}}(Z)) \geq \inf_{V \text{ subspace of } \Lambda^+ \mathcal{F} \setminus \{0\}} \frac{(D_\rho^{\text{DKS}}(Z)u, u)}{\|u\|_{L^2}^2} =: a^+,$$

and

$$\sigma'_{\mathcal{F},1}(D_\rho^{\text{DKS}}(Z)) = \sup_{V \text{ subspace of } \Lambda^- \mathcal{F} \setminus \{0\}} \frac{(D_\rho^{\text{DKS}}(Z)u, u)}{\|u\|_{L^2}^2} =: a^-.$$

The min-max principle can be used if  $a^- < a^+$ . According to Newton's Theorem, we have

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

Consequently,

$$\Lambda^-(D^0 - \frac{\alpha Z}{|x|} + \alpha V_\rho - g'(\rho))\Lambda^- \leq -|D^0|\Lambda^- \leq -\Lambda^-,$$

and according to the Assumption 2.3 and Lemma 3.1,

$$\Lambda^+(D^0 - \frac{\alpha Z}{|x|} + \alpha V_\rho - g'(\rho))\Lambda^+ \geq (1 - \kappa)|D^0|\Lambda^+ > 0.$$

Thus,  $a^- \leq -1 < 0 < a^+$ .

Now we can use the min-max principle. First we consider the non-positive eigenvalues. As  $\sigma'_{\mathcal{F},1}(D_\rho^{\text{DKS}}(Z)) \leq a^- \leq -1$ , we know that there is no eigenvalues in  $(-1, 0]$ .

Next we consider the positive eigenvalues. By the formula (4.1), we know that

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

Similarly, by Lemma 3.1, we know

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

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  $C_{ex}(N)$  and the eigenvalues of the Dirac-Coulomb operator, we know that  $\sigma_{\mathcal{F},k}(Z, N)$  and  $\sigma_{\mathcal{F}}^k(Z, N)$  are continuous with respect to  $Z$  and  $N$ . Besides, they are bounded and non-decreasing with respect to  $k$ .

Finally, we consider the positive essential spectrum. According to the Monotone Convergence Theorem, we know that  $\sigma_{\mathcal{F},ess}(Z, N)$  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.

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  $b \geq \sigma_{\mathcal{F},ess}(Z, N)$ . On the other hand, for any eigenvalue  $\sigma$ , we know that  $\sigma \leq \sigma_{\mathcal{F}}^{ess}(Z, N)$ . Now, we have proved  $b \in [\sigma_{\mathcal{F},ess}(Z, N), \sigma_{\mathcal{F}}^{ess}(Z, N)]$ .

As a result, by the property of the essential spectrum, for any  $\nu < \sigma_{\mathcal{F},ess}(Z, N)$ , there exists a constant  $q \in \mathbb{Z}_+$ , such that

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

which means there are at most  $M$  eigenvalues in the interval  $(0, \nu]$ . This ends the proof.  $\square$

**Lemma 4.1.**

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

Furthermore,

$$\sigma_{H^{1/2},ess}(Z, N) = 1 - C_{ex}(N).$$

*Proof.* Note

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

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

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

On the other hand, we have

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

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,

$$\sigma_{H^{1/2},ess}(Z, N) \leq 1 - C_{ex}(N).$$

It immediately yields the claimed equation.  $\square$

## 5 Existence of solutions

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

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

and consider the following 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 the normalizing conditions

$$\int_0^\infty |u|^2(s) ds = 1. \quad (5.2)$$

Here  $\lambda$  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  $0 \leq \sigma_{H_{m_j, \kappa_j}^{1/2}}^k \leq 1$  independent of  $\rho$  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  $[\sigma_{H_{m_j, \kappa_j, k}^{1/2}}(Z, N), \sigma_{H_{m_j, \kappa_j}^{1/2}}^k(Z, N)]$ . And if  $\sigma_{\rho, k}^{m_j, \kappa_j}(Z) < 1 - C_{ex}(N)$ , it is an eigenvalue.*

*Furthermore, for fixed  $(j, m_j, \kappa_j) \in \mathcal{J}$ , any eigenvalue is single.*



*Proof.* It is an application of the Lemma 2.4, let  $\mathcal{F} = H_{m_j, \kappa_j}^{1/2}$ . First we prove  $H_{m_j, \kappa_j}^{1/2} = \Lambda^+ H_{m_j, \kappa_j}^{1/2} \oplus \Lambda^- H_{m_j, \kappa_j}^{1/2}$ . For any  $u \in H_{m_j, \kappa_j}^{1/2}$ , we know  $U_{m_j, \kappa_j} u = u$ , and  $D^0 u = U_{m_j, \kappa_j} D^{0, m_j, \kappa_j} u$ . Thus,

$$\Lambda^\pm u = U_{m_j, \kappa_j} \left( \frac{1}{2} \pm \frac{D^{0, m_j, \kappa_j}}{|D^{0, m_j, \kappa_j}|} \right) u \in H_{m_j, \kappa_j}^{1/2}.$$

Consequently,  $H_{m_j, \kappa_j}^{1/2} = \Lambda^+ H_{m_j, \kappa_j}^{1/2} \oplus \Lambda^- H_{m_j, \kappa_j}^{1/2}$ . Note

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

and

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

Thus by Lemma 2.4 we get

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

and

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

As  $H_{m_j, \kappa_j}^{1/2} \subset H^{1/2}$ , by Lemma 4.1 we know

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

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

Now, we prove the simplicity of the eigenvalues. It follows from the ODE theories. If not, we assume that  $u$  and  $v$  are two solutions of the equation (5.1) satisfying (5.2) with the same real eigenvalue  $\lambda$  and  $\langle u, v \rangle_{L^2} = 0$ . We fix a point  $r_0 \in (0, \infty)$ . Now, note that by integration by parts

$$\langle D_\rho^{\text{DKS}, m_j, \kappa_j} u, v \rangle_{L^2[r_0, r]} - \langle u, D_\rho^{\text{DKS}, m_j, \kappa_j} v \rangle_{L^2[r_0, r]} = \langle i\sigma_2 u, v \rangle_{\mathbb{C}^2}(r_0) - \langle i\sigma_2 u, v \rangle_{\mathbb{C}^2}(r),$$

where  $\langle \sigma_2 u, v \rangle_{\mathbb{C}^2} = \bar{v}^T \sigma_2 u$  is the inner product for vectors. On the other hand, as they are the eigenfunctions of the same eigenvalue  $\lambda$  we know

$$\langle D_\rho^{\text{DKS}, m_j, \kappa_j} u, v \rangle_{L^2[r_0, r]} - \langle u, D_\rho^{\text{DKS}, m_j, \kappa_j} v \rangle_{L^2[r_0, r]} = 0.$$

Thus,  $\langle i\sigma_2 u, v \rangle_{\mathbb{C}^2}(r) = C$ . Assume that  $u = (u_1, u_2)^T$  and  $v = (v_1, v_2)^T$ . Considering the condition (5.2), we know  $C = 0$ , and  $u_2 \bar{v}_1 - u_1 \bar{v}_2 = 0$ . As a result, there is a function  $c(r)$  such that

$$u_2 = c(r)u_1, \quad v_2 = \overline{c(r)}v_1. \quad (5.3)$$

Let  $F(r) = -\frac{Z}{r} + \frac{\alpha}{r} f_\rho(r) - g'_\rho(r) - (1 + \lambda)$ . Thus, according to equation (5.1), we get

$$\frac{d}{dr} u_1 + \frac{\kappa_j}{r} u_1 + c(r)F(r)u_1 = 0$$

and

$$\frac{d}{dr}v_1 + \frac{\kappa_j}{r}v_1 + \overline{c(r)}F(r)v_1 = 0.$$

Thus,

$$u_1(r) = C_u e^{-\int_{r_0}^r \kappa_j/t - c(t)F(t) dt},$$

and

$$v_1(r) = C_v e^{-\int_{r_0}^r \kappa_j/t - \overline{c(t)}F(t) dt}.$$

As  $\overline{F} = F$  and  $\overline{\kappa_j} = \kappa_j$ , by the expression of  $u_1$  and  $v_1$ , we know that there is a constant  $C'$ , such that

$$v_1 = C'\overline{u_1}. \quad (5.4)$$

As a result  $v_2 = C'\overline{u_2}$  and  $v = C'\overline{u}$ . Hence,  $\overline{u}$  is a solution of equation (5.1) satisfying (5.2) with the eigenvalue  $\lambda$  and  $\langle u, \overline{u} \rangle_{L^2} = 0$ . Thus,  $\Re u \neq 0$  and  $\Im u \neq 0$ . Otherwise, as  $\langle \Re u, \Im u \rangle_{L^2} = 0$ ,

$$\|\Re u\|_{L^2}^2 - \|\Im u\|_{L^2}^2 = \langle u, \overline{u} \rangle_{L^2} = 0.$$

Thus,  $\Im u = \Re u = 0$  and  $u = 0$  which is impossible.

As a result,  $u^{(1)} := \frac{\Re u}{\|\Re u\|_{L^2}}$  and  $u^{(2)} := \frac{\Im u}{\|\Im u\|_{L^2}}$  are two real eigenfunctions satisfying (5.2) with the same eigenvalue  $\lambda$  and

$$\langle u^{(1)}, u^{(2)} \rangle_{L^2} = \frac{1}{2} \Im \langle u, \overline{u} \rangle_{L^2} = 0. \quad (5.5)$$

Repeating the above process and considering the condition (5.2), like equation (5.4) we have  $u^{(2)} = \pm u^{(1)}$ . Thus by equation (5.5),  $u^{(2)} = u^{(1)} = 0$  reaching a contradict. Now, we know the eigenfunction is unique.  $\square$

Recall that  $\sigma_{H^{1/2}}^k(Z, N)$  defined in Lemma 2.4 is the upper bound of the  $k$ -th eigenvalue of operator  $D_0^{\text{DKS}}(Z)$ . Let  $N^*(Z, N) = \max\{k \in \mathbb{Z}_+; \sigma_{H^{1/2}}^k(Z, N) < 1 - C_{ex}(N)\}$ . 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) 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's fixed-point theory we only need the continuity and relative compactness of operator  $\rho_T$ .

Before going further, let  $\sigma(P)$  be the spectrum of the operator  $P$ .

**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  $\rho$ . For any  $u \in H^{1/2}$ , for  $\rho_n \xrightarrow[n \rightarrow \infty]{} \rho$  in  $L^1$  we have

$$(|V_{\rho - \rho_n}|u, u) \leq \frac{\pi}{2} \|\rho - \rho_n\|_{L^1} \| |D^0|^{1/2} u \|_{L^2}^2 \rightarrow 0. \quad (5.6)$$

Now, we consider the exchange-correlation functional. By virtue of the assumption (2.5e) and inequality (3.1), we know

$$\| |g'(\rho) - g'(\rho_n)|^{1/2} u \|_{L^2} \leq C_{g,3}^{1/2} \| |g'(|\rho - \rho_n|)|^{1/2} u \|_{L^2} \leq C_{g,3}^{1/2} C_{ex}(\|\rho - \rho_n\|_{L^1}) \|u\|_{H^{1/2}}. \quad (5.7)$$

Thus,

$$\| |g'(\rho_n) - g'(\rho)|^{1/2} |D^0|^{-1/2} \|_{\mathcal{B}(L^2)} \rightarrow 0. \quad (5.8)$$

Now, combing with the inequality (5.6), (5.7) and Lemma 3.2, we get

$$D_{\rho}^{\text{DKS}}(Z) \leq D_{\rho_n}^{\text{DKS}}(Z) + \left( \frac{\pi}{2} \|\rho - \rho_n\|_{L^1} + C_{g,3} C_{ex}(\|\rho - \rho_n\|_{L^1}) \right) (1 - \kappa)^{-1} |D_{\rho_n}^{\text{DKS}}(Z)|$$

By virtue of the formula (4.1),

$$\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z) \leq \left( 1 + \left( \frac{\pi}{2} \|\rho - \rho_n\|_{L^1} + C_{g,3} C_{ex}(\|\rho - \rho_n\|_{L^1}) \right) \right) (1 - \kappa)^{-1} \sigma_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}}(Z).$$

Similarly, we have

$$\sigma_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}}(Z) \leq \left( 1 + \left( \frac{\pi}{2} \|\rho - \rho_n\|_{L^1} + C_{g,3} C_{ex}(\|\rho - \rho_n\|_{L^1}) \right) \right) (1 - \kappa)^{-1} \sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z).$$

Thus,

$$|\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z) - \sigma_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}}(Z)| \leq \left( \frac{\pi}{2} \|\rho - \rho_n\|_{L^1} + C_{g,3} C_{ex}(\|\rho - \rho_n\|_{L^1}) \right) (1 - \kappa)^{-1} (1 - C_{ex}(N)) \rightarrow 0.$$

Hence we conclude that  $\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z)$  is continuous with respect to  $\rho \in S(N)$ .

By Lemma 5.1, the corresponding eigenfunction  $u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}$  to the eigenvalue  $\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z)$  under the condition (5.2) is unique. Thus, by Cauchy's integral formula, there is a constant  $\epsilon_i$  small enough satisfying

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

and

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

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

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

And as  $\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z)$  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,

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

and

$$\epsilon_i/2 \leq \text{dis}(\sigma(D_{\rho_n}^{\text{DKS}, m_{j_i}, \kappa_{j_i}}(Z)), \partial B(\sigma_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}(Z), \epsilon_i)) \leq \epsilon_i.$$

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

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

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

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

Note

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

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

$$\begin{aligned} & \|(D_{\rho_n}^{\text{DKS}}(Z) - z)^{-1} V_{\rho - \rho_n} (D_{\rho}^{\text{DKS}}(Z) - z)^{-1}\|_{\mathcal{B}(L_{m_{j_i}, \kappa_{j_i}}^2)} \\ & \leq \frac{\pi}{2} \|\rho_n - \rho\|_{L^1} (\|(D_{\rho_n}^{\text{DKS}}(Z) - z)^{-1} |D^0|^{1/2}\|_{\mathcal{B}(L^2)} \|(D_{\rho}^{\text{DKS}}(Z) - z)^{-1} |D^0|^{1/2}\|_{\mathcal{B}(L^2)}) \\ & \leq (1 - \kappa)^{-1} \frac{\pi}{2} \|\rho_n - \rho\|_{L^1} \|(D_{\rho_n}^{\text{DKS}}(Z) - z)^{-1} |D_{\rho_n}^{\text{DKS}}(Z)|^{1/2}\|_{\mathcal{B}(L^2)} \\ & \quad \times \|(D_{\rho}^{\text{DKS}}(Z) - z)^{-1} |D_{\rho}^{\text{DKS}}(Z)|^{1/2}\|_{\mathcal{B}(L^2)} \\ & \leq (1 - \kappa)^{-1} \frac{\pi}{2} \|\rho_n - \rho\|_{L^1} (\epsilon_i^{-1/2} + \epsilon_i^{-1} |z|^{1/2}) (\sqrt{2} \epsilon_i^{-1/2} + \epsilon_i^{-1} 2 |z|^{1/2}) \\ & \leq C \|\rho_n - \rho\|_{L^1}. \end{aligned} \tag{5.9}$$

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

$$\begin{aligned} & \|(D_{\rho_n}^{\text{DKS}}(Z) - z)^{-1} (g'(\rho) - g'(\rho_n)) (D_{\rho}^{\text{DKS}}(Z) - z)^{-1}\|_{\mathcal{B}(L_{m_{j_i}, \kappa_{j_i}}^2)} \\ & \leq C C_{ex}^2 (\|\rho - \rho_n\|_{L^1}). \end{aligned} \tag{5.10}$$

Given

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

by Equation (5.6) and (5.8) for any  $\rho_n \rightarrow \rho$  in  $L^1$  we have

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

Now we have proved that  $T$  is continuous on  $S(N)$ .  $\square$

**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

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

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

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

This implies  $u_{\rho_n, k_i}^{m_{j_i}, \kappa_{j_i}} \rightarrow u_{\rho, k_i}^{m_{j_i}, \kappa_{j_i}}$  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

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

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

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

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,

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

According to Lemma 2.4, 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  $\sigma_{\rho_{n_1}, k_i}^{m_{j_i}, \kappa_{j_i}}(Z)\sigma_{\rho_*, k_i}^{m_{j_i}, \kappa_{j_i}}(Z) < 1 - C_{ex}(N)$  imply that the operators  $(D_{\rho_n}^{\text{DKS}, m_{j_i}, \kappa_{j_i}}(0) - \sigma_{\rho_{n_1}, k_i}^{m_{j_i}, \kappa_{j_i}}(Z))^{-1}$  are uniformly bounded. Hence,

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

As a result,

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

Thus,  $T$  is compact.  $\square$

*Proof of Theorem 2.6.* Now, combing Lemma 5.2 and 5.3 according to the Schauder's fixed point theory, we have proved the existence of a solution set  $(u_{k_i, m_{j_i}, \kappa_{j_i}}, \lambda_{k_i, m_{j_i}, \kappa_{j_i}})_{1 \leq i \leq N}$  for the case  $N \leq N^*(Z, N) = \max\{k \in \mathbb{Z}_+; \sigma_{H^{1/2}}^k(Z, N) < 1 - C_{ex}(N)\}$ . By Lemma 5.1, for any  $1 \leq i \leq N$ ,

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

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

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

Now, we consider the assumption  $N \leq N^*(Z, N) = \max\{k \in \mathbb{Z}_+; \sigma_{H^{1/2}}^k(Z, N) \leq 1 - C_{ex}(N)\}$ . We follow the idea of the proof of Theorem III.3 in [Lio87]. In this case, we approximate  $Z$  by  $Z + \epsilon$ . Thus, as  $\sigma_{H^{1/2}}^k(Z + \epsilon, N) < \sigma_{H^{1/2}}^k(Z, N)$ , we know  $N \leq N^*(Z + \epsilon, N) = \max\{k \in \mathbb{Z}_+; \sigma_{H^{1/2}}^k(Z + \epsilon, N) < 1 - C_{ex}(N)\}$ . Let  $(u_1^\epsilon, \lambda_1^\epsilon, \dots, u_N^\epsilon, \lambda_N^\epsilon)$  be the solution set. Then we have  $u_i^\epsilon \xrightarrow{*} u_i$  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  $u_i^\epsilon$  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 2.6.  $\square$

## 6 Existence of minimizers

*Proof of Theorem 2.8.* From now on, we can prove the existence of minimizers. The following theorem is inspired by the work [HS07]:

**Theorem 6.1.** *Under the Assumptions 2.2 and 2.3 and with the same assumption as in Theorem 2.8, there is a constant  $\nu < \sigma_{H^{1/2}, \text{ess}}(Z, N)$ , 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 (2.6), obviously there is a constant  $\nu < \sigma_{H^{1/2}, \text{ess}}(Z, N)$ , such that

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

By the definition of  $\Gamma_{\text{ps}, Z, N}^+$ , there are at least  $N$  eigenfunctions for the operator  $D_{\rho_\gamma}^{\text{DKS}}(Z)$  if  $\gamma \in \Gamma_{\text{ps}, Z, N}^+$ . 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 3.2, we know

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

By Lemma 2.4 again, we know

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

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. This ends the proof.  $\square$

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

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

By Lemma 3.2, 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

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

and

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

as well as

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

**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

$$\begin{aligned}
\|u_{n,k} - u_k\|_{H^{1/2}} &= \|\nu_{n,k}(D_{\rho_{\gamma_n}}^{\text{DKS}}(Z))^{-1}u_{n,k} - \nu_k(D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1}u_k\|_{H^{1/2}} \\
&\leq C|\nu_k - \nu_{n,k}| + \nu_k\|((D_{\rho_{\gamma_n}}^{\text{DKS}}(Z))^{-1} - (D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1})u_{n,k}\|_{H^{1/2}} \\
&\quad + \nu_k\|(D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1}(u_{n,k} - u_k)\|_{H^{1/2}} \\
&\leq C|\nu_k - \nu_{n,k}| + \nu_k\|(D_{\rho_{\gamma_n}}^{\text{DKS}}(Z))^{-1}V_{\rho_{\gamma_n} - \rho_{\gamma_*}}(D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1}u_{n,k}\|_{H^{1/2}} \\
&\quad + \nu_k\|(D_{\rho_{\gamma_n}}^{\text{DKS}}(Z))^{-1}(g'(\rho_{\gamma_n}) - g'(\rho_{\gamma_*}))(D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1}u_{n,k}\|_{H^{1/2}} \\
&\quad + \nu_k(1 - \kappa)^{-1}\| |D^0|^{-1/2}(u_{n,k} - u_k)\|_{L^2}.
\end{aligned}$$

Similar to the estimates (5.9) and (5.10), we have

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

and

$$\begin{aligned}
&\|(D_{\rho_{\gamma_n}}^{\text{DKS}}(Z))^{-1}(g'(\rho_{\gamma_*}) - g'(\rho_{\gamma_n}))(D_{\rho_{\gamma_*}}^{\text{DKS}}(Z))^{-1}u_{n,k}\|_{L^2} \\
&\leq (1 - \kappa)^{-2}C_{g,3}C_{ex}^2(\|\rho - \rho_n\|_{L^1})\| |D^0|^{-1/2}u_{n,k}\|_{L^2}.
\end{aligned}$$

Consequently, by equations (5.6) and (5.8), we know

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

□

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

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

Given

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

using again the equation (3.1), we yield

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

Finally, we proved

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

The conclusion follows. □



## 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  $\lambda_n$  with  $|\lambda_n|$  non-decreasing, such that

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

Thus, we have

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

□

## B More about the energy criteria (2.6)

In this part, we would like to explain more about the energy criteria.

**Lemma B.1.** *If*

$$(1 + \tau) \sum_{k=1}^N \sigma_{H^{1/2}}^k(Z, N) < (1 - \tau) \sum_{k=1}^{N-1} \sigma_{H^{1/2}, k}(Z, N) + 1 - C_{ex}(N), \quad (\text{B.1})$$

*then the energy criteria (2.6) holds.*

*Proof.* By Lemma 3.2 and Theorem 2.6, we obtain

$$E^{\text{DKS}}(Z, N) \leq (1 + \tau) \inf_{\gamma \in \Gamma_{\text{ps}, Z, N}^+} \text{Tr}_{L^2}(D_{\rho_\gamma}) \leq (1 + \tau) \sum_{k=1}^N \sigma_{H^{1/2}}^k(Z, N). \quad (\text{B.2})$$

On the other hand, by Lemma 4.1, we know  $\sigma_{H^{1/2}, \text{ess}} = 1 - C_{ex}(N)$ , thus the energy criteria holds if

$$(1 + \tau) \sum_{k=1}^N \sigma_{H^{1/2}}^k(Z, N) < (1 - \tau) \sum_{k=1}^{N-1} \sigma_{H^{1/2}, k}(Z, N) + 1 - C_{ex}(N).$$

This ends the proof. □

Now we are going to check whether we could bind one electron ( $N = 1$ ) in our theory for some proper nuclear charges  $Z$ . For simplicity, we only consider the reduced Dirac-Fock model which means  $E_{xc}(\rho) = 0$  for the Dirac-Kohn-Sham model. In this case,

$$\sigma_{H^{1/2},1}(Z, N) = \sigma_1\left(D^0 - \frac{\alpha Z}{|x|}\right) = (1 - \alpha^2 Z^2)^{1/2},$$

$$\sigma_{H^{1/2}}^1(Z, N) = \sigma_1\left(D^0 - \frac{\alpha(Z-1)}{|x|}\right) = (1 - \alpha^2(Z-1)^2)^{1/2}$$

and

$$\tau = \frac{\alpha\pi}{4 - 2\alpha\pi(Z+1)}.$$

We are going to check the inequality:

$$(1 - \alpha^2(Z-1)^2)^{1/2} \left(1 + \frac{\alpha\pi}{4 - 2\alpha\pi(Z+1)}\right) < 1 - \frac{\alpha\pi}{4 - 2\alpha\pi(Z+1)}$$

After simple calculation, this inequality holds for  $26 \leq Z \leq 81$ .

## References

- [AC09] Arnaud Anantharaman and Eric 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.
- [AM12] Carlos Argaez and Michael Melgaard. Existence of a minimizer for the quasi-relativistic kohn–sham model. *Electronic Journal of Differential Equations*, 2012(18):1–20, 2012.
- [BE11] Alexander A Balinsky and William Desmond Evans. *Spectral analysis of relativistic operators*. World Scientific, 2011.
- [CM16] Eric Cancès and Nahia Mourad. Existence of a type of optimal norm-conserving pseudopotentials for kohn–sham models. *Communications in Mathematical Sciences*, 14(5):1315–1352, 2016.
- [CMPS21] Isabelle Catto, Long Meng, Eric Paturel, and Eric Séré. Existence of minimizers for dirac–fock models in crystals. *In preparation*, 2021.
- [DES00] Jean Dolbeault, Maria J Esteban, and Eric Séré. On the eigenvalues of operators with gaps. application to dirac operators. *Journal of Functional Analysis*, 174(1):208–226, 2000.
- [EL13] Weinan E and Jianfeng Lu. *The Kohn–Sham equation for deformed crystals*, volume 221. American Mathematical Soc., 2013.
- [ES99] Maria J Esteban and Eric Séré. Solutions of the dirac–fock equations for atoms and molecules. *Communications in mathematical physics*, 203(3):499–530, 1999.

- [ES01] Maria J Esteban and Eric Séré. Nonrelativistic limit of the dirac-fock equations. In *Annales Henri Poincaré*, volume 2, pages 941–961. Springer, 2001.
- [ES02] Maria J Esteban and Eric Séré. A max-min principle for the ground state of the dirac-fock. In *Mathematical Results in Quantum Mechanics: A Conference on QMATH-8, Mathematical Results in Quantum Mechanics, Universidad Nacional Autónoma de México, Taxco, México, December 10-14, 2001*, volume 307, page 135. American Mathematical Soc., 2002.
- [FG92] G Fang and N Ghoussoub. Second order information on palais-smale sequences in the mountain pass theorem. *Manuscripta mathematica*, 75(1):81–95, 1992.
- [FG94] G Fang and N Ghoussoub. Morse-type information on palais-smale sequences obtained by min-max principles. *Communications on Pure and Applied Mathematics*, 47(12):1595–1653, 1994.
- [FG20] Gero Friesecke and Benedikt Grswald. Existence and nonexistence of homo–lumo excitations in kohn–sham density functional theory. *Nonlinear Analysis*, 200:111973, 2020.
- [Gho93] Nassif Ghoussoub. *Duality and perturbation methods in critical point theory*, volume 107. Cambridge University Press, 1993.
- [Gon14] David Gontier. Existence of minimizers for kohn–sham within the local spin density approximation. *Nonlinearity*, 28(1):57, 2014.
- [HLS09] Christian Hainzl, Mathieu Lewin, and Éric Séré. Existence of atoms and molecules in the mean-field approximation of no-photon quantum electrodynamics. *Archive for rational mechanics and analysis*, 192(3):453–499, 2009.
- [HS07] Matthias Huber and Heinz Siedentop. Solutions of the dirac–fock equations and the energy of the electron-positron field. *Archive for rational mechanics and analysis*, 184(1):1–22, 2007.
- [JGP93] Benny G Johnson, Peter MW Gill, and John A Pople. The performance of a family of density functional methods. *The Journal of chemical physics*, 98(7):5612–5626, 1993.
- [KS65] Walter Kohn and Lu Jeu Sham. Self-consistent equations including exchange and correlation effects. *Physical review*, 140(4A):A1133, 1965.
- [Lev14] Antoine Levitt. Solutions of the multiconfiguration dirac–fock equations. *Reviews in Mathematical Physics*, 26(07):1450014, 2014.
- [Lio87] Pierre-Louis Lions. Solutions of hartree-fock equations for coulomb systems. *Communications in Mathematical Physics*, 109(1):33–97, 1987.
- [LL01] Elliott H Lieb and Michael Loss. Analysis, volume 14 of. *Graduate Studies in Mathematics*, 2001.
- [MV79] Allan Hugh MacDonald and SH Vosko. A relativistic density functional formalism. *Journal of Physics C: Solid State Physics*, 12(15):2977, 1979.

- [Raj78] AK Rajagopal. Inhomogeneous relativistic electron gas. *Journal of Physics C: Solid State Physics*, 11(24):L943, 1978.
- [RC73] AK Rajagopal and J Callaway. Inhomogeneous electron gas. *Physical Review B*, 7(5):1912, 1973.
- [Sér21] Eric Séré. A new definition of the dirac-fock ground state. *In preparation*, 2021.
- [Tha13] Bernd Thaller. *The dirac equation*. Springer Science & Business Media, 2013.
- [WOL72] JAY H WOLKOWISKY. Existence of solutions of the hartree equations for n electrons an application of the schauder-tychonoff theorem. *Indiana University Mathematics Journal*, 22(6):551–568, 1972.