Finiteness of the number of critical values of the Hartree-Fock functional less than a constant smaller than the first energy threshold

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1 Introduction

The eigenvalues of the differential operator called electronic Hamiltonian are central subjects in the research field called quantum chemistry. When we estimate eigenvalues by some method, there exist errors in the estimates. Therefore, to obtain quantitative information of the true eigenvalue we need to have an accurate estimate of the error, which is a very difficult problem. A method which gives an estimate of an eigenvalue having a clear relation to the true eigenvalue is to seek upper and lower bounds of the eigenvalue. Since the true eigenvalue exists between the two bounds, an error estimate is automatically obtained. Because the electronic Hamiltonian is lower semibounded, upper bounds are obtained by variational methods (min-max principle). Lower bounds are much more difficult to obtain and need more future researches. Although there seem to be much more serious difficulties in lower bounds, we consider here a method for upper bounds.

Upper bounds are obtained by the variational method. More precisely we use the min-max principle. Let $\mathcal{H}$ be a Hilbert space and H be lower semibounded selfadjoint operator on $\mathcal{H}$. The min-max principle states that the i-th eigenvalue μ_i in ascending order is identified with the supremum of

$$\inf_{\substack{\Psi\in D(H)\cap X^\perp\\ \|\Psi\|=1}} \langle \Psi, H\Psi\rangle$$

with respect to $(i-1)$-th dimensional subspace X of $\mathcal{H}$. Let V be a closed subspace of $D(H)$. If we define the value $\tilde{\mu}_i$ in the same way replacing $X\subset\mathcal{H}$ and $\Psi\in D(H)\cap X^\perp$ by $X\subset V$ and $\Psi\in V\cap X^\perp$ respectively, we have $\mu_i\le\tilde{\mu}_i$. Thus choosing a finite dimensional subspace V we can calculate an upper bound $\tilde{\mu}_i$ of μ_i practically (Rayleigh-Ritz method). In this method smallness of $\tilde{\mu}_i-\mu_i$ would depend on how close the test function Ψ is to the true eigenfunction. Therefore, it is important to choose the subspace V including a function sufficiently close to the true eigenfunction.

Let us define a functional $\tilde{\mathcal{E}}(\Psi) = \langle \Psi, H\Psi \rangle$ on the unit sphere $\mathbb{S}$ in $\mathcal{H}$. Then the definition of the Fréchet derivative imply that a critical value of $\tilde{\mathcal{E}}$ is an eigenvalue and a critical point is an eigenfunction, and vice varsa. Let μ be a real number such that $\mu_1 < \mu < \mu_2$. Then the set $U_\mu := \{\Psi \in \mathbb{S} : \tilde{\mathcal{E}}(\Psi) < \mu\}$ would be a connected neighborhood in $\mathbb{S}$ of the set A_1 of all eigenfunctions associated with μ_1. If a subset $M \subset \mathbb{S}$ contains a point in U_μ, then a minimizer $\tilde{\Psi}_1$ of $\tilde{\mathcal{E}}$ in M satisfies $\tilde{\Psi}_1 \in U_\mu$. In U_μ the deformation flow of $\tilde{\mathcal{E}}$ would converge to A_1, and therefore, it would be somewhat easy to find a sequence of functions starting from $\tilde{\Psi}_1$ and converging to A_1. Thus if we choose a finite dimensional subspace V containing $\tilde{\Psi}_1$ in the Rayleigh-Ritz method, the upper bound $\tilde{\mu}_1$ would be somewhat close to μ_1.

Let us turn to the case of electronic Hamiltonians. Let $N \in \mathbb{N}$ and $n \in \mathbb{R}$ be the number of electrons and that of nuclei respectively. We denote the positions of electrons and nuclei by $x_i,\ i = 1, \ldots, N$ and $\bar{x}_j,\ j = 1, \ldots, n$ respectively. Let $Z_j,\ j = 1, \ldots, n$ be the atomic numbers of the nuclei. Then the electronic Hamiltonian is written as

$$H := -\sum_{i=1}^{N} \Delta_{x_i} + \sum_{i=1}^{N} V(x_i) + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|},$$

where $V(x) := -\sum_{j=1}^{n} \frac{Z_j}{|x - \bar{x}_j|}$. H is an operator on $L^2(\mathbb{R}^{3N})$. In the Hartree-Fock method we define M by

$$M := \{(N!)^{-1/2} \sum_{\tau \in \mathbf{S}_N} (\operatorname{sgn} \tau) \varphi_1(x_{\tau(1)}) \cdots \varphi_N(x_{\tau(N)}) : \varphi_i \in H^1(\mathbb{R}^3),\ i = 1, \ldots, N$$
$$\langle \varphi_i, \varphi_j \rangle = \delta_{ij},\ i, j = 1, \ldots, N\}.$$

The idea is to consider the product $\varphi_1(x_1) \cdots \varphi_N(x_N)$ which is expected to be a very rough approximation to the eigenfunction. Since it is known that the wave functions for electrons are antisymmetric in physics, we consider the antisymmetrized functions in M. For $\Phi := (\varphi_1, \ldots, \varphi_N)$ we set the Slater determinant

$$\Psi(x_1, \ldots, x_N) := (N!)^{-1/2} \sum_{\tau \in \mathbf{S}_N} (\operatorname{sgn} \tau) \varphi_1(x_{\tau(1)}) \cdots \varphi_N(x_{\tau(N)}). \tag{1.1}$$

The Hartree-Fock (HF) functional $\mathcal{E}(\Phi)$ is defined by $\mathcal{E}(\Phi) := \langle \Psi, H\Psi \rangle$. When we emphasize the number N of electrons, we denote the functional by $\mathcal{E}_N(\Phi)$. The functional $\mathcal{E}(\Phi)$ can be written explicitly as

$$\mathcal{E}(\Phi) = \sum_{i=1}^{N} \langle \varphi_i, h\varphi_i \rangle + \frac{1}{2} \int\int \rho(x) \frac{1}{|x-y|} \rho(y) dx dy - \frac{1}{2} \int\int \frac{1}{|x-y|} |\rho(x,y)|^2 dx dy, \tag{1.2}$$

where $h := -\Delta + V$, $\rho(x) := \sum_{i=1}^{N} |\varphi_i(x)|^2$ is the density, and $\rho(x, y) := \sum_{i=1}^{N} \varphi_i(x) \varphi_i^*(y)$ is the density matrix. Obviously identifying Φ with Ψ by

(1.1), $\mathcal{E}(\Phi)$ is regarded as a restriction of the functional $\tilde{\mathcal{E}}(\Psi) := \langle \Psi, H\Psi \rangle$ on $H^1(\mathbb{R}^{3N})$ to M. As stated above, our purpose is to find a minimizer of $\mathcal{E}(\Phi)$. Since the minimizer is a critical point of $\mathcal{E}(\Phi)$, it satisfies the associated Euler-Lagrange equation which is the Hartree-Fock equation. To consider the variation of $\mathcal{E}(\Phi)$ in M we take the variation of $\mathcal{E}(\Phi)$ with respect to the variation $\varphi_i + \delta\varphi_i,\ i = 1, \ldots, N$ under the constraints $\langle \varphi_i, \varphi_j \rangle = \delta_{ij}$. Then we apply the method of Lagrange multiplier. Let $\epsilon_{ij} \in \mathbb{C},\ 1 \le i, j \le N$ be unknown constants such that (ϵ_{ij}) is an Hermitian matrix. Setting

$$\begin{aligned}\mathcal{G}(\Phi) &:= \mathcal{E}(\Phi) - \sum_{1\le i<j\le N} 2(\mathrm{Re}\,\epsilon_{ij}\mathrm{Re}\,g_{ij}(\Phi) - \mathrm{Im}\,\epsilon_{ij}\mathrm{Im}\,g_{ij}(\Phi)) \\ &= \mathcal{E}(\Phi) - \sum_{1\le i,j\le N} \epsilon_{ij} g_{ij}(\Phi),\end{aligned}$$

with $g_{ij}(\Phi) := \langle \varphi_i, \varphi_j \rangle - \delta_{ij}$ we have

$$\begin{aligned}\delta\mathcal{G} &:= \mathcal{G}(\varphi_1, \ldots, \varphi_i + \delta\varphi_i, \ldots, \varphi_N) - \mathcal{G}(\varphi_1, \ldots, \varphi_i, \ldots, \varphi_N) \\ &= \sum_{i=1}^{N} \langle \delta\varphi_i, \mathcal{F}(\Phi)\varphi_i - \sum_{j=1}^{N} \epsilon_{ij}\varphi_j \rangle + \text{complex conjugate},\end{aligned} \tag{1.3}$$

where the operator $\mathcal{F}(\Phi)$ depending on Φ is given by

$$\mathcal{F}(\Phi) := h + R^{\Phi} - S^{\Phi}.$$

Here the operators R^{Φ} and S^{Φ} are defined by

$$\begin{aligned}R^{\Phi}(x) &:= \sum_{i=1}^{N} \int |x-y|^{-1} |\varphi_i(y)|^2 dy = \sum_{i=1}^{N} Q_{ii}^{\Phi}(x), \\ S^{\Phi} w &:= \sum_{i=1}^{N} \left(\int |x-y|^{-1} \varphi_i^*(y) w(y) dy \right) \varphi_i(x) = \sum_{i=1}^{N} S_{ii}^{\Phi} w,\end{aligned}$$

with

$$\begin{aligned}Q_{ij}^{\Phi}(x) &:= \int |x-y|^{-1} \varphi_j^*(y)\varphi_i(y) dy, \\ (S_{ij}^{\Phi} w)(x) &:= \left(\int \frac{1}{|x-y|} \varphi_j^*(y) w(y) dy \right) \varphi_i(x).\end{aligned}$$

$\mathcal{F}(\Phi)$ is called the Fock operator. By (1.3) the critical points of $\mathcal{E}(\Phi)$ satisfies $\mathcal{F}(\Phi)\varphi_i = \sum_{j=1}^{N} \epsilon_{ij}\varphi_j$. By a unitary transform $\varphi_i^{\mathrm{New}} = \sum a_{ij}\varphi_j^{\mathrm{Old}}$ with an $N \times N$ unitary matrix (a_{ij}) we define new functions φ_i^{New}. Then for a suitable (a_{ij}) the equation

$$\mathcal{F}(\Phi)\varphi_i = \epsilon_i \varphi_i,\ i = 1, \ldots, N \tag{1.4}$$

is satisfied by $(\varphi_1^{\mathrm{New}}, \ldots, \varphi_N^{\mathrm{New}})$ and some $(\epsilon_1, \ldots, \epsilon_N) \in \mathbb{R}^N$. The equation (1.4) (usually with constraints $\langle \varphi_i, \varphi_j \rangle = \delta_{ij}$) is called the Hartree-Fock (HF) equation which has been introduced by Fock [6] and Slater [14]. The constants ϵ_i are unknown, and therefore, (1.4) is a system of nonlinear eigenvalue problem in which we need to find both φ_i and $\epsilon_i,\ i = 1, \dots, N$. The constants ϵ_i are called orbital energies, if the corresponding equation (1.4) has solutions. Since we consider sequences of tuples $(\epsilon_1, \dots, \epsilon_N)$ of orbital energies later, in order to simplify the terminology we call the tuple $(\epsilon_1, \dots, \epsilon_N)$ an orbital energy, if (1.4) has a solution.

It is known that a solution to HF equation which minimizes $\mathcal{E}(\Phi)$ exists (cf. [11]). It is also known that there are infinitely many solutions to HF equation (cf. [12, 10]). In particular it has been proved by Lewin [10] that there exist infinitely many solutions to HF equation associated with critical values of $\mathcal{E}(\Phi)$ less than the first energy threshold

$$J(N-1) := \inf\{\mathcal{E}_{N-1}(\Phi) : \Phi \in \bigoplus_{i=1}^{N-1} H^1(\mathbb{R}^3),\ \langle\varphi_i, \varphi_i\rangle = \delta_{ij},\ 1 \le i, j \le N-1\}. \tag{1.5}$$

Solutions to HF equation are critical points of $\mathcal{E}(\Phi)$ and we are also interested in the associated critical values because they are rough approximations to the eigenvalues of H. In practice, we solve HF equation usually by the self-consistent-field (SCF) method which is a kind of iterative methods (successive approximation) for nonlinear equations. There is no theory to identify the solution obtained by SCF method with a particular critical point and the associated critical value to a particular one. However, if we do not know the structures of the sets of the critical values and the critical points, we can not see what is obtained by SCF method. Here we announce the results about the structures obtained in [3, 4].

Let us finally mention an equation related to HF equation. If we use a product $\varphi_1(x_1)\dots\varphi_N(x_N)$ of functions instead of the antisymmetric function in (1.1), the corresponding Euler-Lagrange equation is called the Hartree equation which has been introduced by Hartree [9]. There are also existence results for the Hartree equation (see e.g. [13, 16, 15, 11, 10]).

2 Fréchet derivative and variational method

Here we recall the definition of the Fréchet derivative. Let X and Y be real Banach spaces, and let U be an open subset of X. A map $f : U \to Y$ is called Fréchet differentiable at $x \in U$, if there exists an operator $A \in \mathcal{L}(X, Y)$ such that

$$\lim_{\|h\|\to 0} \frac{\|f(x+h) - f(x) - Ah\|}{\|h\|} = 0.$$

We call A the Fréchet derivative of f at x, and we denote $A = f'(x)$ or $A(h) = df(x, h)$. If $f'(x_0) = 0$ we call x_0 a critical point of f and $f(x_0)$ a critical value. This condition is equivalent to the following. For any C^1-curve $\gamma : \mathbb{R} \to X$ satisfying $\gamma(0) = x_0$, the derivative of $f(\gamma(t))$ at $t = 0$ is equal to 0. Assume there exist Fréchet derivatives at each point in U. Since $\mathcal{L}(X, Y)$

is a Banach space, we can consider the Fréchet derivative of $f'(x)$ at $y \in U$ which is an element in $\mathcal{L}(X, \mathcal{L}(X, Y))$. $\mathcal{L}(X, \mathcal{L}(X, Y))$ has one-to-one correspondence to the space of the set $\mathcal{L}_2(X, Y)$ of all continuous bilinear maps $B : X \times X \to Y$. In the same way, k-th order derivatives are defined as an element in $\mathcal{L}(X, \mathcal{L}(X, \cdots, \mathcal{L}(X, Y) \cdots))$ which has one-to-one correspondence to the set $\mathcal{L}_k(X, Y)$ of all continuous k-linear maps $B : X \times \cdots \times X \to Y$. We denote the k-th Fréchet derivative of f at x applied to $(h_1, \dots, h_k) \in X \times \cdots \times X$ by $d^k f(x, h_1, \dots, h_k)$. When the mapping from U to $\mathcal{L}(X, \cdots, \mathcal{L}(X, Y) \cdots)$ defined by $x \mapsto d^k f(x, \cdot, \dots, \cdot)$ is continuous, we call f a C^k-functional.

Let f and $g_1, \dots, g_l$ be C^1-functionals on X such that $g_1'(x), \dots, g_l'(x)$ are linearly independent for any $x \in \tilde{M}$, where $\tilde{M}$ is a subset of X defined by $\tilde{M} := \{x \in X : g_1(x) = 0, \dots, g_l(x) = 0\}$. Let us consider $f(x)$ under the constraints $g_1(x) = 0, \dots, g_l(x) = 0$. We call $x_0 \in \tilde{M}$ a critical point and $f(x_0)$ a critical value, if for any C^1-curve $\gamma : \mathbb{R} \to \tilde{M}$ satisfying $\gamma(0) = x_0$ the derivative of $f(\gamma(t))$ at $t = 0$ is equal to 0. Using the implicit function theorem in Banach spaces, we can derive the method of Lagrange multiplier in this case exactly in the same way as in the finite-dimensional case, that is, x_0 is a critical point if and only if there exist constants $\epsilon_1, \dots, \epsilon_l \in \mathbb{R}$ such that x_0 is a critical point of the functional $f(x) - \epsilon_1 g_1(x) - \cdots - \epsilon_l g_l(x)$ without restriction. Notice that in the derivation of HF equation the functions $g_{ij}(\Phi) := \langle \varphi_i, \varphi_j \rangle - \delta_{ij}$ in the constraints are complex-valued, and therefore, the Lagrange multipliers are complex-valued. However, since $g_{ij}(\Phi) = g_{ji}^*(\Phi)$ the constraints $g_{ij}(\Phi) = 0$ and $g_{ji}(\Phi) = 0$ are not independent, and choosing ϵ_{ij} satisfying $\epsilon_{ij} = \epsilon_{ji}^*$ we can make $\mathcal{E}(\Phi) - \sum_{ij} \epsilon_{ij} g_{ij}$ a real-valued functional.

If a critical point of f satisfies a differential equation, we call the equation the Euler-Lagrange equation associated with f. By the method of Lagrange multiplier we can see that the Euler-Lagrange equation associated with a functional f with constraints $g_1(x) = 0, \dots, g_l(x) = 0$ contains unknown constants $\epsilon_1, \dots, \epsilon_l$ which are Lagrange multipliers. Therefore, we need to determine both the solution to the equation and the constants. We call such a problem an eigenvalue problem. When the Euler-Lagrange equation is nonlinear, we call it nonlinear eigenvalue problem. HF equation is obtained applying the method of Lagrange multiplier to HF functional as in Section 1. Solving HF equation is a nonlinear eigenvalue problem, and since there are N^2 constraints for N functions, it is a system of nonlinear equations with unknown constants.

3 Main results

The critical values of HF functional below the first energy threshold $J(N-1)$ defined by (1.5) are similar to isolated eigenvalues of linear operators in the sense of following theorems obtained by [3, 4].

Theorem 3.1 ([3])**.** *For any $\epsilon > 0$ the set of all critical values of HF functional* (1.2) *less than $J(N-1) - \epsilon$ is finite.*

Let us consider the SCF method. In SCF method first, we choose an initial function $\Phi^0 = {}^t(\varphi_1^0, \ldots, \varphi_N^0)$. Next we continue an iterative procedure until the sequence $\{\Phi^j\}$ of the functions obtained in the procedure converges. In the iterative procedure, we find N eigenfunctions $\varphi_1^{j+1}, \ldots, \varphi_N^{j+1}$ of $\mathcal{F}(\Phi^j)$ associated with N lowest eigenvalues (including multiplicity) $\mu_1^{j+1}, \ldots, \mu_N^{j+1}$ and set the next function $\Phi^{j+1} := {}^t(\varphi_1^{j+1}, \ldots, \varphi_N^{j+1})$. We consider cases in which Φ^j converges in $\bigoplus_{i=1}^N H^1(\mathbb{R}^3)$ in the following corollary.

Corollary 3.2. *For any $\epsilon > 0$ the set of all critical values of the HF functional* (1.2) *obtained by SCF method with the initial function Φ^0 satisfying $\mathcal{E}(\Phi^0) < J(N-1) - \epsilon$ is finite.*

The set of all critical points has more complicated structure than that of critical values. We can see the reason from the following simple example. Let $f : \mathbb{R}^2 \to \mathbb{R}$ be defined by $f(x, y) = x^2$. Then f has only one critical value 0. However the set of critical points is $\{(0, y) : y \in \mathbb{R}\}$. From this example we can see that since there are many critical points associated with a critical value, the structure of the set of critical points is complicated.

For the second theorem we introduce some standard definitions. We call a Hausdorff space M a real-analytic manifold, if for some $n \in \mathbb{N}$, M is locally homeomorphic to n-dimensional Euclidean space and its coordinate transformations are real-analytic. We call a subset A of a real-analytic manifold M a real-analytic subsets, if there exists an open cover $\{U_i\}$ of M such that for any i there exist real-analytic functions $f_i^1, \ldots, f_i^s$ on U_i satisfying $A \cap U_i = \{z \in U_i : f_i^1(z) = \cdots = f_i^s(z) = 0\}$. Let $A(E)$ be the set of all solutions to HF equation (1.4) with constraints $\langle \varphi_i, \varphi_j \rangle = \delta_{ij}$ associated with a critical value E of HF functional (Recall that HF equation is the Euler-Lagrange equation associated with HF functional). We have the following theorem and corollary for the set of critical points.

Theorem 3.3 ([4])**.** *For any $E < J(N-1)$, $A(E)$ has a structure as a union of a finite number of real-analytic subsets of a finite number of compact real-analytic manifolds without isolated points.*

The real analytic manifolds in Theorem 3.3 can be regarded as a subset of $\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$. For a subspace X of $\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$ let us denote by P_X the orthogonal projection onto X.

Corollary 3.4. *Let $E < J(N-1)$. Then for any $\delta > 0$ there exists a finite-dimensional subspace X_δ of $\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$ such that $\|P_{X_\delta^\perp} \Phi\|_{\bigoplus_{i=1}^N L^2(\mathbb{R}^3)} < \delta$, $\forall \Phi \in A(E)$, where $X_\delta^\perp$ is the orthogonal subspace of X_δ. Moreover, for a real-analytic manifold $\tilde{A}(E)$ which appears in Theorem 3.3 we can choose X_δ such that $P_{X_\delta} \tilde{A}(E)$ is a real-analytic closed submanifold of X_δ.*

Remark 3.5. *(1) By Corollary 3.4 we can see that for the approximation of all solutions in $A(E)$ up to errors less than δ we have only to approximate the subspace X_δ, and it is not necessary to take a dense basis of functions in $\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$.*

(2) *Although $\tilde{A}(E)$ is locally homeomorphic to a finite-dimensional Euclidean space, it may not be included in any finite-dimensional subspace of $\bigoplus_{i=1}^{N} H^2(\mathbb{R}^3)$. We can make an example of a subset of infinite dimensional Hilbert space $\mathcal{H}$ locally homeomorphic to a finite-dimensional Euclidean subspace and not included in any finite-dimensional subspace of $\mathcal{H}$ as follows. Let $f_i : B \to B,\ i = 1, 2, \dots$ be homeomorphisms, where B is a unit ball in $\mathbb{R}^k$ for some $k \in \mathbb{N}$. Set*

$$M := \{(f_1(x), 2^{-1}f_2(x), \dots, 2^{-n}f_n(x), \dots) \in l^2 : x \in B\}. \tag{3.1}$$

Then M is homeomorphic to B. We also set subsets of finite-dimensional spaces

$$M_n := \{(f_1(x), 2^{-1}f_2(x), \dots, 2^{-n}f_n(x)) \in \mathbb{R}^{kn} : x \in B\}.$$

Let V_n be a one-dimensional subspace of $\mathbb{R}^{kn}$ such that $V_n \cap M_n$ is composed of more than two elements. Since $\mathbb{R}^{kn}$ is finite-dimensional and M_n has infinitely many points, such a subspace V_n exists. Let us choose two points $x, y \in B$ such that $g_n(x), g_n(y) \in V_n \cap M_n$, where

$$g_n(x) := (f_1(x), 2^{-1}f_2(x), \dots, 2^{-n}f_n(x)).$$

We can choose f_{n+1} such that $f_{n+1}(x)$ and $f_{n+1}(y)$ are linearly independent in $\mathbb{R}^k$. For any $A \subset \mathbb{R}^m$ let us denote by $\dim A$ the minimum of dimension of the linear subspaces of $\mathbb{R}^m$ including A. Then we can see that $\dim M_{n+1} \geq \dim M_n + 1$. If we choose f_n in this way, M in (3.1) has infinitely many linearly independent elements, and therefore it can not be included in any finite-dimensional subspace of l^2.

Although, HF equation can not be solved exactly, we have the same result as Theorems 3.1 and 3.3 even if we assume the potential $\sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}$ between electrons were 0. In this case the equation corresponding to HF equation is a system of linear eigenvalue problems, and we can determine critical values and critical points explicitly. Let us also assume $n = 1$, $Z_1 = 1$, $\bar{x}_1 = 0$ and $N = 2$. Then the equation is written as

$$\begin{aligned} &(-\Delta - \frac{1}{|x_i|})\varphi_i = \epsilon_i \varphi_i,\ i = 1, 2, \\ &\|\varphi_i\| = 1,\ i = 1, 2, \\ &\langle \varphi_1, \varphi_2 \rangle = 0. \end{aligned}$$

We can explicitly calculate $J(N-1) = J(1)$ as $J(N-1) = -\frac{1}{4}$, and the critical values less than $J(N-1)$ are

$$-\frac{1}{4} - \frac{1}{4j^2},\ j = 2, 3, \dots.$$

The set of all solutions to the equation associated with the lowest critical value $-\frac{5}{16}$ is

$$A(-\frac{5}{16}) = (\mathbb{S}^1 \times \mathbb{S}^7) \sqcup (\mathbb{S}^7 \times \mathbb{S}^1).$$

For any $(\varphi_1, \varphi_2) \in \mathbb{S}^1 \times \mathbb{S}^7$ we have $(\varphi_2, \varphi_1) \in \mathbb{S}^7 \times \mathbb{S}^1$. These two solutions give the same Slater determinant (1.1) except for sign.

When we introduce spin, the same functions in $\mathbb{R}^3$ with different spin are orthogonal. Thus in this case the critical values and the critical points are different from the case without spin. The critical values less than $J(N-1)$ are

$$-\frac{1}{4} - \frac{1}{4j^2},\ j = 1, 2, \ldots.$$

The set of solutions to the equation associated with the lowest critical value $-\frac{1}{2}$ is

$$A(-\frac{1}{2}) = \mathbb{S}^1 \times \mathbb{S}^1.$$

4 Compactness of sets of solutions to HF equation

In the proof of the main theorems, compactness of sets of solutions to HF equation plays a central role. For the proof we need to prove convergence in $L^2(\mathbb{R}^3)$. Let Ω be a bounded region in $\mathbb{R}^3$. If $H^1(\mathbb{R}^3)$ is replaced by $H^1(\Omega)$, compactness of a set of functions in $L^2(\Omega)$ follows from the boundedness in $H^1(\Omega)$ by Rellich selection theorem. In order to prove the convergence in $L^2(\mathbb{R}^3)$ we need uniform decay of the solutions.

We can obtain a uniform exponential decay for solutions whose orbital energies are bounded. The method of the proof is essentially Agmon's one for linear Schrödinger equations (cf. [1]). We regard the nonlinear terms such as

$$\left(\int |x-y|^{-1} \varphi_j^*(y) \varphi_i(y) dy \right) \varphi_j(x),$$

and

$$\left(\int |x-y|^{-1} \varphi_j^*(y) \varphi_j(y) dy \right) \varphi_i(x),$$

as functions φ_j and φ_i multiplied by potentials $Q_{ji}(x) = \int |x-y|^{-1} \varphi_j^*(y) \varphi_i(y) dy$ and $Q_{jj}(x) \int |x-y|^{-1} \varphi_j^*(y) \varphi_j(y) dy$ respectively. For the proof of the uniform decay we need uniform decay of these potentials which is attained by a weak decay condition on φ_i. We also need uniform boundedness of solutions with respect to $\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$-norm as in the following lemma. Note that if $\Phi \in \bigoplus_{i=1}^N H^1(\mathbb{R}^3)$ satisfies HF equation, we have $\Phi \in \bigoplus_{i=1}^N H^2(\mathbb{R}^3)$ by the standard regularity result (cf. [12]). The following lemma is easily obtained by the Δ-boundedness of the Coulomb potential.

Lemma 4.1. *Let $d > 0$ be a constant. Then there exists a constant $C_d > 0$ such that any solution $\Phi = {}^t(\varphi_1, \ldots, \varphi_N)$ of HF equation* (1.4) *associated with an orbital energy $(\epsilon_1, \ldots, \epsilon_N) \in (-d, d)^N$ satisfies*

$$\|\Delta \varphi_i\| < C_d,\ 1 \le i \le N.$$

Set $B_r := \{x \in \mathbb{R}^3 : |x| < r\}$. Using Lemma 4.1 we obtain the following exponential decay by Agmon's method.

Lemma 4.2. *Let $\epsilon > \tilde{\epsilon} > 0$, $d, r_0 > 0$ and C_d be the constant in Lemma 4.1. Then there exists $\tilde{C} > 0$ such that for any solution $\Phi = {}^t(\varphi_1, \ldots, \varphi_N)$ of HF equation (1.4) associated with an orbital energy $(\epsilon_1, \ldots, \epsilon_N) \in (-d, -\epsilon)^N$ and satisfying $\|\varphi_i\|_{L^2(\mathbb{R}^3 \setminus B_{r_0})} < \frac{\epsilon - \tilde{\epsilon}}{8NC(C_d+1)}$, $1 \le i \le N$ the following estimate holds.*

$$\|\exp(\tilde{\epsilon}^{1/2}|x|)\varphi_i(x)\| \le \tilde{C},\ 1 \le i \le N.$$

Idea of the proof. We first prove weak decay estimate for Q^{Φ}_{ij}. For $|y| < |x|/2$ we can easily see that $|x-y|^{-1} \to 0$ as $|x| \to \infty$. On the other hand, for $|y| \ge |x|/2$ $\varphi_i(y)$ decays as $|x| \to \infty$. Here we note by Lemma 4.1 and the relative Δ-boundedness of $|x|^{-1}$, there exists a constant $C > 0$ independent of Φ such that the following inequality holds.

$$\||x-y|^{-1}\varphi_i\|_{L^2(\mathbb{R}^3_y)} \le C(\|\Delta\varphi_i\| + \|\varphi_i\|) \le C(C_d + 1).$$

Thus we have

$$\begin{aligned}\left|\int_{|y|\ge|x|/2} |x-y|^{-1}\varphi_j^*(y)\varphi_i(y)dy\right| &\le \||x-y|^{-1}\varphi_i(y)\|_{L^2(\mathbb{R}^3_y)}\|\varphi_j\|_{L^2(\mathbb{R}^3\setminus B_{|x|/2})}\\ &\le C(C_d+1)\|\varphi_j\|_{L^2(\mathbb{R}^3\setminus B_{|x|/2})} \le \frac{\epsilon - \tilde{\epsilon}}{8N},\end{aligned}$$

where we used the assumption in the third inequality. Combining the estimates in the two regions $|y| < |x|/2$ and $|y| \ge |x|/2$ it follows that there exists a constant $r_0 > 0$ such that

$$|Q^{\Phi}_{ij}(x)| < \frac{\epsilon - \tilde{\epsilon}}{4N}, \tag{4.1}$$

holds for $|x| > r_0$.

The idea of Agmon's method is to multiply a exponential weight to the equation, take a innerproduct with the solution itself and take its real part. Since we do not know the integrability of the function multiplied by the exponential weight in advance, we multiply a cut-off function to the exponent and take the limit as the support of the cut-off function spreads after the calculation. Let $\eta(r) \in C_0^\infty(\mathbb{R})$ be a function such that $\eta(r) = r$ for $-1 < r < 1$ and $|\eta'(r)| \le 1$. Set $\rho_k(x) := \tilde{\epsilon}^{1/2}k\eta(\langle x\rangle/k)$ and $\chi_k(x) := e^{\rho_k(x)}$, where $\langle x\rangle := \sqrt{1+|x|^2}$. By a direct calculation we have

$$\begin{aligned}\mathrm{Re}\,\langle(-\Delta\varphi_i), \chi_k^2\varphi_i\rangle &= \|\nabla(\chi_k\varphi_i)\|^2 - \|(\nabla\chi_k)\varphi_i\|^2\\ &= \|\nabla(\chi_k\varphi_i)\|^2 - \|(\nabla\rho_k)\chi_k\varphi_i\|^2\\ &\ge -\|(\nabla\rho_k)\chi_k\varphi_i\|^2 \ge -\tilde{\epsilon}\|\chi_k\varphi_i\|^2,\end{aligned}$$

where we used $|\nabla\rho_k|^2 < \tilde{\epsilon}$ in the last step. Thus when we multiply χ_k^2 to HF equation $(\mathcal{F}(\Phi) - \epsilon_i)\varphi_i = 0$, take the innerproduct with φ_i and take the real part, we obtain

$$0 = \mathrm{Re}\,\langle\varphi_i, \chi_k^2(\mathcal{F}(\Phi) - \epsilon_i)\varphi_i\rangle \ge (-\epsilon_i - \tilde{\epsilon})\|\chi_k\varphi_i\|^2 + \text{remainder},$$

where the remainder term includes $Q_{ij}^{\Phi}(x)$ which decays as $|x| \to \infty$ as in (4.1). Moreover, since $\epsilon_i < -\epsilon$, we have $-\epsilon_i - \tilde{\epsilon} > 0$. In a bounded region the weight is bounded and estimated by a constant. Thus summing the inequality for all i we can see that there exists a constants $r_1 > 0$ and $C > 0$ independent of Φ such that

$$(\epsilon - \tilde{\epsilon})/2 \sum_{i=1}^{N} \int_{|x|>r_1} |\chi_k \varphi_i(x)|^2 dx < C. \tag{4.2}$$

Since by Fatou's lemma we have

$$\liminf_{k\to\infty} \sum_{i=1}^{N} \int_{|x|>r_1} |\chi_k \varphi_i(x)|^2 dx \geq \sum_{i=1}^{N} \int_{|x|>r_1} |e^{\tilde{\epsilon}^{1/2}\langle x \rangle} \varphi_i(x)|^2 dx,$$

the lemma follows from (4.2). □

Using Lemma 4.2 we can prove the compactness of the set of solutions to HF equation associated with orbital energies less than a negative constant. In fact the compactness holds also for the set of solutions without the orthogonality constraints $\langle \varphi_i, \varphi_j \rangle = 0,\ i \neq j$ and with the normalization constraints $\langle \varphi_i, \varphi_i \rangle = 1,\ i = 1, \ldots, N$ only. This fact is crucial in the proof of Theorem 3.3. The compactness in this sense follows from the following lemma.

Lemma 4.3 ([4, Lemma 3.4]). *Let $\Phi^m := {}^t(\varphi_1^m, \ldots, \varphi_N^m)$ be solutions to HF equation* (1.4) *associated with $\mathbf{e}^m := (\epsilon_1^m, \ldots, \epsilon_N^m),\ m = 1, 2, \ldots,$ with the normalization constraints $\langle \varphi_i, \varphi_i \rangle = 1,\ 1 \leq i \leq N$ and not necessarily satisfying the orthogonality constraints $\langle \varphi_i, \varphi_j \rangle = 0,\ i \neq j$. Assume $\mathbf{e}^m$ converges to $\mathbf{e}^\infty := (\epsilon_1^\infty, \ldots, \epsilon_N^\infty) \in (-\infty, 0)^N$. Then there exists a subsequence of Φ^m converging in $\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$ to a solution of HF equation with the constraints $\langle \varphi_i, \varphi_i \rangle = 1,\ 1 \leq i \leq N$ associated with $\mathbf{e}^\infty$.*

Sketch of the proof. Since $\{\mathbf{e}^m\}$ is converging to $\mathbf{e}^\infty := (\epsilon_1^\infty, \ldots, \epsilon_N^\infty) \in (-\infty, 0)^N$, it is bounded and there exist constants $\epsilon, d > 0$ such that $\mathbf{e}^m \in (-d, -\epsilon)^N$ for sufficiently large m. Without loss of generality we can assume this condition is satisfied by any m. Thus by Lemma 4.1 there exists a constant $C > 0$ such that $\|\Phi^m\|_{\bigoplus_{i=1}^N H^2(\mathbb{R}^3)} < C$ for any m. Therefore, by the Rellich selection theorem we can see that for any $k \in \mathbb{N}$ there exists a Cauchy subsequence of $\{\varphi_i^m\}$ in $L^2(B_1)$. We construct subsequences $\{\varphi_i^{m_{k,l}}\}_l,\ k = 0, 1, \ldots$ of $\{\varphi_i^m\}$ by the the mathematical induction in the following way. Let $\{\varphi_i^{m_{0,l}}\}_l = \{\varphi_i^l\}_l$. Assume $\{\varphi_i^{m_{k,l}}\}_l$ has been constructed. Then we chose a Cauchy subsequence of $\{\varphi_i^{m_{k,l}}\}_l$ in $L^2(B_{k+1})$ and denote it by $\{\varphi_i^{m_{k+1,l}}\}_l$. The Cauchy sequence $\{\varphi_i^{m_{k,l}}\}_l$ satisfies

$$\|\varphi_i^{m_{k,l}} - \varphi_i^{m_{k,l'}}\|_{L^2(B_k)} \to 0,\ i = 1, \ldots, N,$$

as $l, l' \to \infty$. Hence we can choose $l_k \in \mathbb{N}$ such that

$$\|\varphi_i^{m_{k,l}} - \varphi_i^{m_{k,l'}}\|_{L^2(B_k)} < k^{-1},\ i = 1, \ldots, N,$$

holds for $l, l' \geq l_k$. Then the subsequence $\{\varphi_i^{m_{k,l_k}}\}_k$ of $\{\varphi_i^m\}$ satisfies

$$\|\varphi_i^{m_{k,l_k}} - \varphi_i^{m_{k',l_{k'}}}\|_{L^2(B_{k_0})} < k_0^{-1},$$

where $k_0 := \min\{k, k'\}$. Thus we may assume from the beginning of the proof that $\{\varphi_i^k\}$ itself is a sequence satisfying

$$\|\varphi_i^k - \varphi_i^{k'}\|_{L^2(B_{k_0})} < k_0^{-1}. \tag{4.3}$$

Using the constraint $\|\varphi_i^k\| = 1$ and (4.3), we can see that for any $\delta > 0$ there exist $r_0 > 0$ and $l_0 \in \mathbb{N}$ such that $\|\varphi_i^k\|_{L^2(\mathbb{R}^3 \setminus B_{r_0})} = (1 - \|\varphi_i^k\|^2_{L^2(B_{r_0})})^{1/2} < \delta$, $\forall k > l_0$. Thus the assumption in Lemma 4.2 is satisfied for some $\tilde{\epsilon}, r_0$ and for φ_i^k with sufficiently large k. Therefore, noticing $\langle x\rangle \exp(-\tilde{\epsilon}^{1/2}|x|)$ is bounded. we can see that there exists a constant $\tilde{C} > 0$ such that $\|\langle x\rangle \varphi_i^k\| < \tilde{C}$ holds for any k and i. Since $|x| \geq k$ for $x \in \mathbb{R}^3 \setminus B_k$, we have

$$\|\varphi_i^k\|_{L^2(\mathbb{R}^3 \setminus B_k)} \leq k^{-1}\|\langle x\rangle \varphi_i^k\| \leq \tilde{C}k^{-1}.$$

Therefore, we obtain

$$\begin{aligned}\|\varphi_i^{k_1} - \varphi_i^{k_2}\|_{L^2(\mathbb{R}^3)} &\leq \|\varphi_i^{k_1} - \varphi_i^{k_2}\|_{L^2(B_{k_0})} + \|\varphi_i^{k_1} - \varphi_i^{k_2}\|_{L^2(\mathbb{R}^3 \setminus B_{k_0})} \\ &\leq k_0^{-1} + 2\tilde{C}k_0^{-1}.\end{aligned}$$

for sufficiently large k_0. Thus $\{\varphi_i^k\}$ is a Cauchy sequence in $L^2(\mathbb{R}^3)$.

Using the Δ-boundedness of $|x|^{-1}$ and Lemma 4.1. we can easily see that there exist constants $C_1, C_2 > 0$ independent of k_1 and k_2 such that

$$|Q_{ij}^{k_1}(x) - Q_{ij}^{k_2}(x)| \leq C_1 \sum_{l=1}^{N} \|\varphi_l^{k_1} - \varphi_l^{k_2}\|,$$

$$|R^{k_1}(x) - R^{k_2}(x)| \leq C_2 \sum_{l=1}^{N} \|\varphi_l^{k_1} - \varphi_l^{k_2}\|.$$

Moreover we can easily see that there exists a constant $C_3 > 0$ such that

$$|Q_{ij}^k(x)|, |R^k(x)| < C_3, \ \forall k \in \mathbb{N}$$

for any k. Thus using HF equation (1.4) we can see that there exists $C_4 > 0$ such that

$$\begin{aligned}&\|h(\varphi_i^{k_1} - \varphi_i^{k_2})\| \\ &\quad = \left\|(\epsilon_i^{k_1} - R^{k_1}(x))\varphi_i^{k_1} + \sum_{j=1}^{N} Q_{ij}^{k_1}(x)\varphi_j^{k_1} - (\epsilon_i^{k_2} - R^{k_2}(x))\varphi_i^{k_2} - \sum_{j=1}^{N} Q_{ij}^{k_2}(x)\varphi_j^{k_2}\right\| \\ &\quad \leq C_4 \sum_{l=1}^{N} \|\varphi_l^{k_1} - \varphi_l^{k_2}\| + |\epsilon_i^{k_1} - \epsilon_i^{k_2}|.\end{aligned} \tag{4.4}$$

Because V is Δ-bounded with relative bound smaller than 1, Δ is h-bounded. Therefore, by (4.4) we can see that $\{\varphi_i^k\}$ is a Cauchy sequence in $H^2(\mathbb{R}^3)$. Let $\varphi_i^\infty \in H^2(\mathbb{R}^3)$ be the limit. Then the both sides of HF equation converge in $L^2(\mathbb{R}^3)$ and setting $\Phi^\infty := (\varphi_1^\infty, \ldots, \varphi_N^\infty)$ we have

$$h\varphi_i^\infty + R^{\Phi^\infty}\varphi_i^\infty - \sum_{j=1}^N Q_{ij}^{\Phi^\infty}\varphi_j^\infty = \epsilon_i^\infty \varphi_i^\infty,$$

which completes the proof. □

Let $\epsilon > 0$ be an arbitrary constant. We consider the compactness of the set of all solutions to HF equation whose orbital energies satisfying the condition $\mathbf{e} \in (-\infty, -\epsilon]^N$. By Lemma 4.3 the compactness of the set of solutions follows from convergence of a subsequence of the orbital energies $\mathbf{e}^m$ which follows from the boundedness of $\mathbf{e}^m$. Since an upper bound $-\epsilon$ is given by the assumption, we need only a lower bound which is given by the following lemma.

Lemma 4.4. *Any orbital energy $\mathbf{e} = (\epsilon_1, \ldots, \epsilon_N)$ of HF equation (1.4) with the constraints $\langle \varphi_i, \varphi_i \rangle = 1,\ 1 \le i \le N$ and not necessarily satisfying the constraints $\langle \varphi_i, \varphi_j \rangle = 0,\ i \ne j$ satisfies $\epsilon_i \ge \inf \sigma(h) > -\infty,\ 1 \le i \le N$, where $\sigma(h)$ is the spectra of h.*

Proof. We shall prove

$$R^\Phi - S^\Phi \ge 0. \tag{4.5}$$

as an inequality for operators. Since we can write $R^\Phi - S^\Phi = \sum_{i=1}^N (Q_{ii}^\Phi - S_{ii}^\Phi)$, we only need to prove

$$Q_{ii}^\Phi - S_{ii}^\Phi \ge 0,\ 1 \le i \le N.$$

Let $w \in L^2(\mathbb{R}^3)$. We define

$$\hat{\Psi}_i := 2^{-1/2}(w(x)\varphi_i(y) - \varphi_i(x)w(y)).$$

Then it is easily seen that

$$\langle w, (Q_{ii}^\Phi - S_{ii}^\Phi)w \rangle = \int \frac{1}{|x-y|} |\hat{\Psi}_i|^2 dxdy \ge 0.$$

Hence we have (4.5). Therefore $\mathcal{F}(\Phi) = h + R^\Phi - S^\Phi \ge h$. Since by the definition ϵ_i^m is an eigenvalue of $\mathcal{F}(\Phi)$, we obtain $\epsilon_i^m \ge \inf \sigma(h)$. □

By Lemma 4.4 and the arguments above the lemma we obtain the following theorem.

Theorem 4.5. *For any $\epsilon > 0$, the set of all solutions to HF equation associated with orbital energies $\mathbf{e} \in (-\infty, -\epsilon]^N$ with constraints $\langle \varphi_i, \varphi_j \rangle = \delta_{ij},\ i, j = 1, \ldots, N$ or $\langle \varphi_i, \varphi_i \rangle = 1,\ i = 1, \ldots, N$ is a compact set in $\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$.*

Using Koopmans' well-known theorem (cf. Remark 4.8) we can prove that if Φ is a solution to HF equation associated with an ortbtal energy $\mathbf{e} = (\epsilon_1, \ldots, \epsilon_N)$ with constraints $\langle \varphi_i, \varphi_j \rangle = \delta_{ij},\ i, j = 1, \ldots, N$ and $\mathcal{E}_N(\Phi) \le J(N-1) - \epsilon$, then we have $\epsilon_i \le -\epsilon,\ i = 1, \ldots, N$, where $J(N-1)$ is defined by (1.5). Thus for any $\epsilon > 0$ the set of all solutions with constraints $\langle \varphi_i, \varphi_j \rangle = \delta_{ij},\ i, j = 1, \ldots, N$ associated with critical values less than or equal to $J(N-1) - \epsilon$ is a compact set. Actually, this holds also for constraints $\langle \varphi_i, \varphi_i \rangle = 1,\ i = 1, \ldots, N$ which is important in the proof of Theorem 3.3. In order to prove the compactness for this constraints we need the following lemma.

Lemma 4.6. *Let $\tilde{J}(N-1)$ be defined by*

$$\tilde{J}(N-1) := \inf\{\mathcal{E}_{N-1}(\Phi) : \Phi \in \bigoplus_{i=1}^{N-1} H^1(\mathbb{R}^3),\ \langle \varphi_i, \varphi_i \rangle = 1,\ 1 \le i \le N-1\}.$$

Then $\tilde{J}(N-1) = J(N-1)$.

Sketch of the proof. Since the set for $\tilde{J}(N-1)$ in which we take the infimum includes that for $J(N-1)$, we have $\tilde{J}(N-1) \le J(N-1)$. For the opposite inequality we only need to prove that for any $\tilde{\Phi} = {}^t(\tilde{\varphi}_1, \ldots, \tilde{\varphi}_{N-1}) \in \bigoplus_{i=1}^{N-1} H^1(\mathbb{R}^3)$ satisfying $\langle \tilde{\varphi}_i, \tilde{\varphi}_i \rangle = 1,\ 1 \le i \le N-1$, there exists $\Phi = {}^t(\varphi_1, \ldots, \varphi_{N-1}) \in \bigoplus_{i=1}^{N-1} H^1(\mathbb{R}^3)$ satisfying $\langle \varphi_i, \varphi_j \rangle = \delta_{ij},\ 1 \le i, j \le N-1$ such that

$$\mathcal{E}_{N-1}(\tilde{\Phi}) \ge \mathcal{E}_{N-1}(\Phi). \tag{4.6}$$

If $\tilde{\varphi}_i,\ i = 1, \ldots, N-1$ are linearly dependent, then $\mathcal{E}(\tilde{\Phi}) = 0$. Since $J(N-1)$ is negative (cf [10]), it is obvious Φ satisfying (4.6) exists. When φ_i are linearly independent, we transform $\tilde{\Phi}$ by a unitary matrix U to $\hat{\Phi} := {}^t(\hat{\varphi}_1, \ldots, \hat{\varphi}_{N-1})$ by $\hat{\varphi}_i := \sum_j U_{ji}\tilde{\varphi}_j$ such that $\langle \hat{\varphi}_i, \hat{\varphi}_j \rangle = \lambda_i \delta_{ij}$ with $0 < \lambda_i \le 1$. We set $\Phi = (\varphi_1, \ldots, \varphi_N) := (\lambda_1^{-1/2}\hat{\varphi}_1, \ldots, \lambda_N^{-1/2}\hat{\varphi}_N)$. Then Φ satisfies the constraints $\langle \varphi_i, \varphi_j \rangle = \delta_{ij}$. We define the Slater determinants $\hat{\Psi}$ and Ψ of $\hat{\Phi}$ and Φ as

$$\begin{aligned} \hat{\Psi}(x_1, \ldots, x_N) &= (N!)^{-1/2} \sum_{\tau \in \mathbf{S}_N} (\operatorname{sgn} \tau) \hat{\varphi}_1(x_{\tau(1)}) \cdots \hat{\varphi}_N(x_{\tau(N)}), \\ \Psi(x_1, \ldots, x_N) &= (N!)^{-1/2} \sum_{\tau \in \mathbf{S}_N} (\operatorname{sgn} \tau) \varphi_1(x_{\tau(1)}) \cdots \varphi_N(x_{\tau(N)}) \\ &= \left(\prod_{i=1}^{N} \lambda_i^{-1/2} \right) \hat{\Psi}. \end{aligned}$$

Noticing $\lambda_i > 0$, $\langle \hat{\Psi}, H\hat{\Psi} \rangle = \mathcal{E}_{N-1}(\hat{\Phi}) < 0$ and $\langle \hat{\Psi}, H\hat{\Psi} \rangle = \left(\prod_{i=1}^{N} \lambda_i \right) \langle \Psi, H\Psi \rangle$ we have $\langle \Psi, H\Psi \rangle < 0$. Thus noting $\lambda_i \le 1$,

$$\mathcal{E}_{N-1}(\tilde{\Phi}) = \mathcal{E}_{N-1}(\hat{\Phi}) = \langle \hat{\Psi}, H\hat{\Psi} \rangle = \left(\prod_{i=1}^{N} \lambda_i \right) \langle \Psi, H\Psi \rangle \ge \langle \Psi, H\Psi \rangle = \mathcal{E}_{N-1}(\Phi),$$

which completes the proof. □

For any $E \in \mathbb{R}$ we denote by $\tilde{A}(E)$ the set of all solutions Φ to HF equation with constraints $\langle \varphi_i, \varphi_i \rangle = 1,\ i = 1, \ldots, N$ such that $\mathcal{E}(\Phi) = E$. By Lemma 4.6 and Koopmans' theorem we obtain the following lemma.

Lemma 4.7. *For any $E < J(N-1)$, $\tilde{A}(E)$ is a compact set in $\bigoplus_{i=1}^{N} H^2(\mathbb{R}^3)$.*

Proof. Let $\Phi \in \tilde{A}(E)$. Without loss of generality, we may assume $\epsilon_N = \max\{\epsilon_1, \ldots, \epsilon_N\}$. The Hartree-Fock functional can be written as

$$\mathcal{E}_N(\Phi) = \sum_{j=1}^{N} \langle \varphi_j, h\varphi_j \rangle + \sum_{1 \le i < j \le N} (J_{ij} - K_{ij}),$$

where

$$J_{ij} := \int\int |\varphi_i(x)|^2 \frac{1}{|x-y|} |\varphi_j(y)|^2 dxdy,$$
$$K_{ij} := \int\int \varphi_i^*(x)\varphi_j(x) \frac{1}{|x-y|} \varphi_j^*(y)\varphi_i(y) dxdy.$$

Here we used that $J_{jj} = K_{jj}$ and thus $J_{jj} - K_{jj}$ vanishes. A direct calculation also yields

$$\epsilon_N = \langle \varphi_N, \mathcal{F}(\Phi)\varphi_N \rangle = \langle \varphi_N, h\varphi_N \rangle + \sum_{i=1}^{N-1} (J_{iN} - K_{iN}).$$

Therefore, setting $\tilde{\Phi} := {}^t(\varphi_1, \ldots, \varphi_{N-1})$ we can see that

$$\begin{aligned}
\mathcal{E}_N(\Phi) = &\sum_{j=1}^{N-1} \langle \varphi_j, h\varphi_j \rangle + \sum_{1 \le i < j \le N-1} (J_{ij} - K_{ij}) \\
&+ \langle \varphi_N, h\varphi_N \rangle + \sum_{i=1}^{N-1} (J_{iN} - K_{iN}) \\
&= \mathcal{E}_{N-1}(\tilde{\Phi}) + \epsilon_N \ge \tilde{J}(N-1) + \epsilon_N.
\end{aligned}$$

By Lemma 4.6 this implies that if $\mathcal{E}_N(\Phi) \le J(N-1) - \epsilon$, then $\epsilon_N \le -\epsilon$. Thus if Φ^m is a sequence of solutions to HF equation such that $\mathcal{E}(\Phi) = E < J(N-1)$ with constraints $\langle \varphi_i, \varphi_i \rangle = 1,\ i = 1, \ldots, N$, their orbital energies $\mathbf{e}^m = (\epsilon_1^m, \ldots, \epsilon_N^m)$ satisfy $\epsilon_i^m \le E - J(N-1) < 0$. Therefore, by Theorem 4.5 there exists a subsequence of Φ^m converging to a solution Φ^∞ to HF equation. By the continuity of $\mathcal{E}(\Phi)$ we can see that $\mathcal{E}(\Phi^\infty) = E$, which means the compactness of $\tilde{A}(E)$. □

Remark 4.8. *The equality $\mathcal{E}_N(\Phi) = \mathcal{E}_{N-1}(\tilde{\Phi}) + \epsilon_N$ is called Koopmans' theorem and well-known, because it gives an interpretation of $-\epsilon_N$ as a rough approximation $\mathcal{E}_{N-1}(\tilde{\Phi}) - \mathcal{E}_N(\Phi)$ to the ionization potential.*

5 Auxiliary functional

We have seen in the previous section that the compactness of the set of solutions to HF equation holds also for the case with the constraints $\langle \varphi_i, \varphi_i \rangle = 1,\ i = 1, \ldots, N$. This set of constraints is easier to handle because it is satisfied by critical points $[\Phi, \mathbf{e}] \in (\bigoplus_{i=1}^N H^2(\mathbb{R}^3)) \bigoplus \mathbb{R}^N$ of a functional $f : (\bigoplus_{i=1}^N H^2(\mathbb{R}^3)) \bigoplus \mathbb{R}^N \to \mathbb{R}$ defined below. The Lagrange multiplier $\mathbf{e}$ of the original problem is included in the variable of the functional f.

Denote by $Y_1 := (\bigoplus_{i=1}^N H^2(\mathbb{R}^3)) \bigoplus \mathbb{R}^N$ and $Y_2 := (\bigoplus_{i=1}^N L^2(\mathbb{R}^3)) \bigoplus \mathbb{R}^N$ the direct sums of real Banach spaces regarding the sets $H^2(\mathbb{R}^3)$ and $L^2(\mathbb{R}^3)$ of complex-valued functions as real Banach spaces with respect to multiplication by real numbers. We define a functional $f : Y_1 \to \mathbb{R}$ by

$$f(\Phi, \mathbf{e}) := \mathcal{E}(\Phi) - \sum_{i=1}^N \epsilon_i (\|\varphi_i\|^2 - 1).$$

To consider the Fréchet derivative of f we define a bilinear form $\langle\langle \cdot, \cdot \rangle\rangle$ on Y_1 and Y_2 by

$$\langle\langle [\Phi^1, \mathbf{e}^1], [\Phi^2, \mathbf{e}^2] \rangle\rangle := \sum_{i=1}^N 2\mathrm{Re}\, \langle \varphi_i^1, \varphi_i^2 \rangle + \sum_{i=1}^N \epsilon_i^1 \epsilon_i^2,$$

where $[\Phi^j, \mathbf{e}^j] \in Y_j,\ j = 1, 2$ with $\Phi^j = {}^t(\varphi_1^j, \ldots, \varphi_N^j)$ and $\mathbf{e}^j = (\epsilon_1^j, \ldots, \epsilon_N^j)$. We also define a mapping $F : Y_1 \to Y_2$ by

$$F(\Phi, \mathbf{e}) := [{}^t(F_1(\Phi, \mathbf{e}), \ldots, F_N(\Phi, \mathbf{e})), (1 - \|\varphi_1\|^2, \ldots, 1 - \|\varphi_N\|^2)],$$

where $F_i(\Phi, \mathbf{e}) := \mathcal{F}(\Phi)\varphi_i - \epsilon_i \varphi_i$. Then we can see that if $\Phi = {}^t(\varphi_1, \ldots, \varphi_N)$ is a solution to HF equation satisfying the constraints $\langle \varphi_i, \varphi_i \rangle = 1,\ 1 \le i \le N$ and $\mathbf{e}$ is the associated orbital energy, $F(\Phi, \mathbf{e}) = 0$ holds. Moreover, by a direct calculation we have

$$df([\Phi, \mathbf{e}], [\tilde{\Phi}, \tilde{\mathbf{e}}]) = \langle\langle [\tilde{\Phi}, \tilde{\mathbf{e}}], F(\Phi, \mathbf{e}) \rangle\rangle.$$

Thus $[\Phi, \mathbf{e}]$ is a critical point of f, if and only if $F(\Phi, \mathbf{e}) = 0$, i.e. if and only if Φ is a solution to HF equation associated with the orbital energy $\mathbf{e}$ with constraints $\langle \varphi_i, \varphi_i \rangle = 1,\ 1 \le i \le N$.

6 Real-analytic operators in Banach space

Here we introduce the notion of real-analyticity of mappings between Banach spaces used in the proof of the main theorem.

Definition 6.1. *Let D be an open subset of X. The mapping $F : D \to Y$ is said to be real-analytic on D if the following conditions are fulfilled:*

(i) For each $x \in D$ there exist Fréchet derivatives of arbitrary orders $d^m F(x, \ldots)$.

(ii) For each $x \in D$ there exists $\delta > 0$ such that for any $h \in X$ satisfying $\|h\| < \delta$ one has

$$F(x+h) = \sum_{m=0}^{\infty} \frac{1}{m!} d^m F(x, h^m), \tag{6.1}$$

(the convergence being locally uniform and absolute), where $h^m := [h, \dots, h]$ (m-times).

A composition of two real-analytic operators is also real-analytic (see Proposition 3 in [8] and the sentences below the proposition).

We call a functional $f : X \to \mathbb{R}$ is real-analytic, if f is real-analytic in the sense of Definition 6.1 with $Y = \mathbb{R}$. HF functional $\mathcal{E}(\Phi)$ and the auxiliary functional $f(\Phi, \mathbf{e})$ in Section 5 are real-analytic functionals on $\bigoplus_{i=1}^N H^1(\mathbb{R}^3)$ and $Y_1 = (\bigoplus_{i=1}^N H^2(\mathbb{R}^3)) \bigoplus \mathbb{R}^N$ respectively. We can see this from the fact that in (6.1) up to only fourth order terms appear and direct calculations.

For real-analytic operators the following real-analytic version of the implicit function theorem in Banach spaces holds.

Lemma 6.2 ([8, Theorem 3R])**.** *Let X, Y, Z be real Banach spaces, $G \subset X \times Y$ an open set and $[x_0, y_0] \in G$. Let $F : G \to Z$ be a real-analytic mapping such that $[F'_y(x_0, y_0)]^{-1}$ exists and $F(x_0, y_0) = 0$. (We denote by*

$$F'_y(x_0, y_0)h = \lim_{t \to 0} [F(x_0, y_0 + th) - F(x_0, y_0)]/t,$$

for $h \in Y$ the partial derivative by y. Under our assumptions this derivative exists in the Fréchet sense.)

Then there exist a neighborhood $U(x_0)$ in X of the point x_0 and a neighborhood $U(y_0)$ in Y of the point y_0 such that $U(x_0) \times U(y_0) \subset G$ and there exists one and only one mapping $y : U(x_0) \to U(y_0)$ for which $F(x, y(x)) = 0$ on $U(x_0)$. Moreover, y is a real-analytic mapping on $U(x_0)$.

The phrase "only one" in the lemma indicate that for $x \in U(x_0)$ there exists a unique $y \in U(y_0)$ such that $F(x, y) = 0$.

7 Proof of Theorem 3.1 and Corollary 3.2

Theorem 3.1 follows easily from the following theorem by Koopmans' theorem (cf. Remark 4.8). For any $\epsilon > 0$ let $\Gamma(\epsilon)$ be the set of all critical values of HF functional $\mathcal{E}(\Phi)$ associated with orbital energies satisfying $\epsilon_i < -\epsilon,\ 1 \le i \le N$.

Theorem 7.1. *For any $\epsilon > 0$, $\Gamma(\epsilon)$ is finite.*

Let us see how Theorem 3.1 follows from 7.1. By Koopmans' theorem we have

$$\mathcal{E}_N(\Phi) = \mathcal{E}_{N-1}(\tilde{\Phi}) + \epsilon_N \ge J(N-1) + \epsilon_N,$$

where $\tilde{\Phi}$ is as in the proof of Lemma 4.7. Hence if $\mathcal{E}_N(\Phi) < J(N-1) - \epsilon$, then $\epsilon_N < -\epsilon$. Therefore, by Theorem 7.1 we can see that the set of all critical values $\mathcal{E}_N(\Phi)$ satisfying $\mathcal{E}_N(\Phi) < J(N-1) - \epsilon$ is finite, which is the result in Theorem 3.1.

Now our purpose is to prove Theorem 7.1. For the proof we need the following lemma in Fučik-Nečas-Souček-Souček [7].

Lemma 7.2 ([7, Theorem 4.1])**.** *Let f be a real-analytic functional on a Banach space Y_1 and let Y_2 be another Banach space. Suppose that there exists a bilinear form $\langle\langle \cdot, \cdot \rangle\rangle$ on $Y_1 \times Y_2$ such that for fixed $y \in Y_1$, $\langle\langle y, \cdot \rangle\rangle$ is continuous on Y_2 and $\langle\langle y, x \rangle\rangle = 0$ for all $y \in Y_1$ implies $x = 0$. For each $y \in Y_1$ suppose there exists $F(y)$ such that*

(f1) $df(y, h) = \langle\langle h, F(y) \rangle\rangle$ *for each* $h \in Y_1$.

Let the operator

(f2) $F : Y_1 \to Y_2$ *is real-analytic.*

Denote $\mathcal{B}_f := \{y \in Y_1 : f'(y) = 0\}$ *and let* $y_0 \in \mathcal{B}_f$. *Suppose that*

(f3)

$$F'(y_0) = L + M,$$

where L is an isomorphism of Y_1 onto Y_2 and M is a compact operator.

Then there exists a neighborhood $U(y_0)$ in Y_1 of a point y_0 such that $f(\mathcal{B}_f \cap U(y_0))$ is a one-point set.

Proof of Theorem 7.1. Theorem 7.1 is proved by contradiction. More precisely, we show that the existence of infinitely many critical values $\mathcal{E}(\Phi^n)$, $\mathcal{E}(\Phi^n) \neq \mathcal{E}(\Phi^m)$, $n \neq m$ associated with orbital energies $\mathbf{e}^n := (\epsilon_1^n, \dots, \epsilon_N^n) \in (-\infty, -\epsilon)^N$, $n = 1, 2, \dots$ leads to a contradiction. First, by Theorem 4.5 and Lemma 4.4 we find a converging subsequence $[\Phi^{m_k}, \mathbf{e}^{m_k}]$ of $[\Phi^m, \mathbf{e}^m]$ whose limit point is denoted by $[\Phi^\infty, \mathbf{e}^\infty]$ which is a pair of solution to HF equation and the associated orbital energy. Clearly we have $\epsilon_i^\infty \leq -\epsilon$, where $\mathbf{e}^\infty = (\epsilon_1^\infty, \dots, \epsilon_N^\infty)$. Note also that $[\Phi^m, \mathbf{e}^m]$ is a critical point of f in Section 5 and $f(\Phi^{m_k}, \mathbf{e}^{m_k}) \to f(\Phi^\infty, \mathbf{e}^\infty)$. Moreover, noticing $f(\Phi^m, \mathbf{e}^m) = \mathcal{E}(\Phi^m)$ we have $f(\Phi^m, \mathbf{e}^m) \neq f(\Phi^n, \mathbf{e}^n)$, $m \neq n$. Next we show that at $[\Phi^\infty, \mathbf{e}^\infty]$ the mapping F in Section 5 satisfies $F'(\Phi^\infty, \mathbf{e}^\infty) = L + M$, where L is an isomorphism and M is a compact operator. Thus by Lemma 7.2 there exists a neighborhood U of $[\Phi^\infty, \mathbf{e}^\infty]$ such that the set of critical value of f in U is one point set, which contradicts $f(\Phi^{m_k}, \mathbf{e}^{m_k}) \to f(\Phi^\infty, \mathbf{e}^\infty)$.

Let us prove $F'(\Phi^\infty, \mathbf{e}^\infty) = L + M$. First, we consider the first half components of F consisting of functions. We define $\tilde{F} : \bigoplus_{i=1}^N H^2(\mathbb{R}^3) \to \bigoplus_{i=1}^N L^2(\mathbb{R}^3)$ by

$$\tilde{F}(\Phi) := {}^t(F_1(\Phi, \mathbf{e}^\infty), \dots, F_N(\Phi, \mathbf{e}^\infty)).$$

$\tilde{F}$ is a vector-valued function whose components are functions. The variable Φ of F also has N components $\varphi_i,\ i=1,\dots,N$. Therefore, the Fréchet derivative of $\tilde{F}$ is a matrix of operators written as

$$\tilde{F}'(\Phi)=\begin{pmatrix} [F_1]'_1(\Phi) & [F_1]'_2(\Phi) & \cdots & [F_1]'_N(\Phi) \\ [F_2]'_1(\Phi) & [F_2]'_2(\Phi) & \cdots & [F_2]'_N(\Phi) \\ \vdots & & & \vdots \\ [F_N]'_1(\Phi) & [F_N]'_2(\Phi) & \cdots & [F_N]'_N(\Phi) \end{pmatrix},$$

where $[F_i]'_j(\Phi)\in\mathcal{L}(H^2(\mathbb{R}^3),L^2(\mathbb{R}^3))$ is defined by

$$\begin{aligned}&[F_i]'_j(\Phi)w\\ &\quad:=\lim_{t\to 0}[F_i(\varphi_1,\dots,\varphi_j+tw,\dots,\varphi_N,\mathbf{e}^\infty)-F_i(\varphi_1,\dots,\varphi_j,\dots,\varphi_N,\mathbf{e}^\infty)]/t,\end{aligned}$$

for any $w\in H^2(\mathbb{R}^3)$. Here a matrix B whose components are $B_{ij}\in\mathcal{L}(H^2(\mathbb{R}^3)$ $,L^2(\mathbb{R}^3))$ acts on $W=(w_1,\dots,w_N)\in\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$ as $(BW)_i=\sum_{j=1}^N B_{ij}w_j$. In other words, for any $W:=(w_1,\dots,w_N)\in\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$ we have

$$d\tilde{F}(\Phi,W)=\begin{pmatrix} \sum_{j=1}^N [F_1]'_j(\Phi)w_j \\ \sum_{j=1}^N [F_2]'_j(\Phi)w_j \\ \vdots \\ \sum_{j=1}^N [F_N]'_j(\Phi)w_j \end{pmatrix}.$$

Hereafter, we consider the derivative at Φ^∞ and we omit dependence of Fréchet derivative on Φ. That is, for a mapping $G:\bigoplus_{i=1}^N H^2(\mathbb{R}^3)\to L^2(\mathbb{R}^3)$ and $w\in H^2(\mathbb{R}^3)$ we denote by

$$G'_j w:=\lim_{t\to 0}[G(\varphi_1^\infty,\dots,\varphi_j^\infty+tw,\dots,\varphi_N^\infty)-G(\varphi_1^\infty,\dots,\varphi_j^\infty,\dots,\varphi_N^\infty)]/t,\quad (7.1)$$

the partial derivative of G by w at Φ^∞. Here let us remember $F_i(\Phi,\mathbf{e})=\mathcal{F}(\Phi)\varphi_i-\epsilon_i\varphi_i$ and $\mathcal{F}(\Phi):=h+R^\Phi-S^\Phi$. We consider the Fréchet derivative of $F_i(\Phi,\mathbf{e}^\infty)$ with respect to the variable Φ. For the calculation of $[F_i(\Phi,\mathbf{e}^\infty)]'_j$ we rewrite $F_i(\Phi,\mathbf{e}^\infty)$ as follows. Let us define

$$R_i^\Phi(x):=\sum_{j\neq i}\int |x-y|^{-1}\varphi_j^*(y)\varphi_j(y)dy=\sum_{j\neq i}Q_{jj}^\Phi(x),$$

and

$$S_i^\Phi:=\sum_{j\neq i}S_{jj}^\Phi.$$

Then by $Q_{ii}^\Phi\varphi_i=S_{ii}^\Phi\varphi_i$, $F_i(\Phi,\mathbf{e}^\infty)=\mathcal{F}(\Phi)\varphi_i-\epsilon_i^\infty\varphi_i$ is rewritten as

$$F_i(\Phi,\mathbf{e}^\infty)=h\varphi_i+R_i^\Phi\varphi_i-S_i^\Phi\varphi_i-\epsilon_i^\infty\varphi_i.\quad (7.2)$$

Thus we have

$$[F_i]'_j=\delta_{ij}(h-\epsilon_i^\infty)+[R_i^\Phi\varphi_i]'_j-[S_i^\Phi\varphi_i]'_j.\quad (7.3)$$

Let us consider the Fréchet derivatives in the equation (7.3). By direct calculations we have

$$\begin{aligned} [R_i^\Phi \varphi_i]'_i &= R_i^{\Phi^\infty}, \\ [R_i^\Phi \varphi_i]'_j &= S_{ij}^{\Phi^\infty} + \bar{S}_{ij}^{\Phi^\infty},\ j \neq i, \end{aligned} \tag{7.4}$$

and

$$\begin{aligned} [S_i^\Phi \varphi_i]'_i &= S_i^{\Phi^\infty}, \\ [S_i^\Phi \varphi_i]'_j &= Q_{ij}^{\Phi^\infty} + \bar{S}_{ji}^{\Phi^\infty},\ j \neq i, \end{aligned} \tag{7.5}$$

where

$$(\bar{S}_{ij}^\Phi w)(x) := \left(\int |x-y|^{-1} w^*(y) \varphi_j(y) dy \right) \varphi_i(x).$$

We define mappings

$$\mathcal{R}, \mathcal{Q} : \bigoplus_{i=1}^N H^2(\mathbb{R}^3) \to \bigoplus_{i=1}^N L^2(\mathbb{R}^3),$$

by

$$\begin{aligned} (\mathcal{R}W)_i &:= R_i^{\Phi^\infty} w_i, \\ (\mathcal{Q}W)_i &:= \sum_{j \neq i} Q_{ij}^{\Phi^\infty} w_j. \end{aligned}$$

Then we have $\mathcal{R} - \mathcal{Q} \geq 0$, which plays a crucial role in the proof of the theorem. Let $W := {}^t(w_1, \ldots, w_N) \in \bigoplus_{i=1}^N L^2(\mathbb{R}^3)$ We use the notation $[\tilde{i}\tilde{j}|kl]$ defined by

$$[\tilde{i}\tilde{j}|kl] := \int |x-y|^{-1} w_i^*(x) w_j(x) (\varphi_k^\infty)^*(y) \varphi_l^\infty(y) dx dy,$$

where indices such as $\tilde{i}$ indicate that φ_i is replaced by w_i. Then by a straightforward calculation we obtain

$$\langle W, (\mathcal{R} - \mathcal{Q})W \rangle = \sum_{i=1}^N \sum_{j \neq i} \{ [\tilde{i}\tilde{i}|jj] - [\tilde{i}\tilde{j}|ji] \}.$$

On the other hand, we can calculate as

$$\begin{aligned} &2^{-1} \sum_{i=1}^N \sum_{j \neq i} \int dx_1 dx_2 |x_1 - x_2|^{-1} |w_i(x_1) \varphi_j^\infty(x_2) - w_j(x_1) \varphi_i^\infty(x_2)|^2 \\ &= 2^{-1} \sum_{i=1}^N \sum_{j \neq i} \{ [\tilde{i}\tilde{i}|jj] + [\tilde{j}\tilde{j}|ii] - [\tilde{i}\tilde{j}|ji] - [\tilde{j}\tilde{i}|ij] \} \\ &= \sum_{i=1}^N \sum_{j \neq i} \{ [\tilde{i}\tilde{i}|jj] - [\tilde{i}\tilde{j}|ji] \} \\ &= \langle W, (\mathcal{R} - \mathcal{Q})W \rangle. \end{aligned}$$

Since the left-hand side is obviously positive, we can see that $\mathcal{R} - \mathcal{Q} \geq 0$.

Next we consider a decomposition of $\delta_{ij}(h - \epsilon_i^\infty)$ in (7.3). For this purpose it is more appropriate to regard $\delta_{ij}(h - \epsilon_i^\infty)$ as a matrix

$$\mathcal{H} := \begin{pmatrix} h - \epsilon_1^\infty & 0 & 0 & \cdots & 0 & 0 \\ 0 & h - \epsilon_2^\infty & 0 & \cdots & 0 & 0 \\ \vdots & & & & & \vdots \\ 0 & 0 & 0 & \cdots & 0 & h - \epsilon_N^\infty \end{pmatrix} = \mathrm{diag}\,(h - \epsilon_1^\infty, \ldots, h - \epsilon_N^\infty),$$

where $\mathrm{diag}\,(A_1, \ldots, A_N)$ is the diagonal matrix whose diagonal elements are $A_1, \ldots, A_N$. Then we have a decomposition $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$, where

$$\mathcal{H}_1 := \mathrm{diag}\,(h(1 - E(-\epsilon/2)) - \epsilon_1^\infty, \ldots, h(1 - E(-\epsilon/2)) - \epsilon_N^\infty),$$

and

$$\mathcal{H}_2 := \mathrm{diag}\,(hE(-\epsilon/2), \ldots, hE(-\epsilon/2)),$$

where $E(\lambda)$ is the resolution of identity of h. Since $\epsilon_i^\infty \leq -\epsilon$, we have

$$\mathcal{H}_1 \geq \epsilon/2,$$

as an inequality of operators. On the other hand, since $\inf \sigma_{ess}(h) = 0$, $\mathcal{H}_2$ is a compact operator. The remaining operators in $\tilde{F}'$ are expressed by $\mathcal{S}$ and $\bar{\mathcal{S}}$ defined by

$$(\mathcal{S}W)_i = \sum_{j \neq 1} S_{ij}^{\Phi^\infty} w_j - S_i^{\Phi^\infty} w_i, \ (\bar{\mathcal{S}}W)_i = \sum_{j \neq 1} \bar{S}_{ij}^{\Phi^\infty} w_j,$$

which are finite dimensional and hence compact operators. Now we have the decomposition

$$\tilde{F}'(\Phi^\infty) = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{R} - \mathcal{Q} + \mathcal{S} + \bar{\mathcal{S}} - {}^t\bar{\mathcal{S}} = \mathcal{L} + \mathcal{M},$$

where $\mathcal{L} := \mathcal{H}_1 + \mathcal{R} - \mathcal{Q}$ and $\mathcal{M} := \mathcal{H}_2 + \mathcal{S} + \bar{\mathcal{S}} - {}^t\bar{\mathcal{S}}$. By $\mathcal{H}_1 \geq \epsilon/2$ and $\mathcal{R} - \mathcal{Q} \geq 0$ we have $\mathcal{L} \geq \epsilon/2$. Thus 0 is in the resolvent set of $\mathcal{L}$ and therefore, $\mathcal{L}$ is an isomorphism from $\bigoplus_{i=1}^N H^2(\mathbb{R})$ onto $\bigoplus_{i=1}^N L^2(\mathbb{R})$. On the other hand, $\mathcal{M}$ is obviously a compact operator.

We define a mapping $\hat{F} : \mathbb{R}^N \to \bigoplus_{i=1}^N L^2(\mathbb{R})$ by

$$\hat{F}(\mathbf{e}) := {}^t(F_1(\Phi^\infty, \mathbf{e}), \ldots, F_N(\Phi^\infty, \mathbf{e})),$$

Then we can easily see that

$$\begin{aligned} &F'(\Phi^\infty, \mathbf{e}^\infty)[\Phi, \mathbf{e}] \\ &\quad = [\tilde{F}'(\Phi^\infty)\Phi + \hat{F}'(\mathbf{e}^\infty)\mathbf{e}, -2\mathrm{Re}\,\langle \varphi_1, \varphi_1^\infty \rangle, \ldots, -2\mathrm{Re}\,\langle \varphi_N, \varphi_N^\infty \rangle] \\ &\quad = L[\Phi, \mathbf{e}] + M[\Phi, \mathbf{e}], \end{aligned}$$

where

$$L[\Phi, \mathbf{e}] := [\mathcal{L}\Phi, \mathbf{e}],$$
$$M[\Phi, \mathbf{e}] := [\mathcal{M}\Phi - \mathbf{e}\Phi^{\infty}, -2\mathrm{Re}\,\langle\varphi_1, \varphi_1^{\infty}\rangle - \epsilon_1, \ldots, -2\mathrm{Re}\,\langle\varphi_N, \varphi_N^{\infty}\rangle - \epsilon_N].$$

Here $\mathbf{e}\Phi^{\infty} := {}^t(\epsilon_1\varphi_1^{\infty}, \ldots, \epsilon_N\varphi_N^0)$. It is easy to see that L is an isomorphism and M is a compact operator, which has been our goal. □

Proof of Corollary 3.2. For the proof we introduce an auxiliary functional on $(\bigoplus_{i=1}^N H^2(\mathbb{R}^3)) \oplus (\bigoplus_{i=1}^N H^2(\mathbb{R}^3))$ with orthonormal constraints as in [5]. For $\Phi = {}^t(\varphi_1, \ldots, \varphi_N) \in \bigoplus_{i=1}^N H^2(\mathbb{R}^3)$ and $\tilde{\Phi} = {}^t(\tilde{\varphi}_1, \ldots, \tilde{\varphi}_N) \in \bigoplus_{i=1}^N H^2(\mathbb{R}^3)$ satisfying $\langle\varphi_i, \varphi_j\rangle = \delta_{ij}$ and $\langle\tilde{\varphi}_i, \tilde{\varphi}_j\rangle = \delta_{ij}$ we define

$$\begin{aligned}
\mathcal{E}(\Phi, \tilde{\Phi}) &:= \sum_{i=1}^N \langle\varphi_i, h\varphi_i\rangle + \sum_{i=1}^N \langle\tilde{\varphi}_i, \mathcal{F}(\Phi)\tilde{\varphi}_i\rangle \\
&= \sum_{i=1}^N \langle\varphi_i, h\varphi_i\rangle + \sum_{i=1}^N \langle\tilde{\varphi}_i, h\tilde{\varphi}_i\rangle \\
&\quad + \int\int \rho(x)\frac{1}{|x-y|}\tilde{\rho}(y)dxdy - \int\int \frac{1}{|x-y|}\rho^*(x,y)\tilde{\rho}(x,y)dxdy,
\end{aligned}$$

where $\tilde{\rho}(x) := \sum_{i=1}^N |\tilde{\varphi}_i(x)|^2$ and $\tilde{\rho}(x,y) := \sum_{i=1}^N \tilde{\varphi}_i(x)\tilde{\varphi}_i^*(y)$. Then in SCF procedure Φ^{j+1} minimizes the functional $\mathcal{E}(\Phi^j, \Phi)$ of Φ, i.e. $\inf_{\langle\varphi_i,\varphi_j\rangle=\delta_{ij}} \mathcal{E}(\Phi^j, \Phi) = \mathcal{E}(\Phi^j, \Phi^{j+1})$. Thus we have $\mathcal{E}(\Phi^j, \Phi^{j+1}) \le \mathcal{E}(\Phi^j, \Phi^{j-1})$ and $\mathcal{E}(\Phi^j, \Phi^{j+1}) \le \mathcal{E}(\Phi^j, \Phi^j)$. Since $\mathcal{E}(\Phi, \tilde{\Phi})$ is symmetric with respect to Φ and $\tilde{\Phi}$, we obtain $\mathcal{E}(\Phi^j, \Phi^{j+1}) \le \mathcal{E}(\Phi^{j-1}, \Phi^j)$. Therefore, if Φ^j converges to a critical point Φ^{∞}, we have

$$2\mathcal{E}(\Phi^0) = \mathcal{E}(\Phi^0, \Phi^0) \ge \mathcal{E}(\Phi^j, \Phi^{j+1}) \to \mathcal{E}(\Phi^{\infty}, \Phi^{\infty}) = 2\mathcal{E}(\Phi^{\infty}).$$

Thus if $\mathcal{E}(\Phi^0) < J(N-1) - \epsilon$, then $\mathcal{E}(\Phi^{\infty}) < J(N-1) - \epsilon$. Hence by Theorem 3.1 it follows that the critical value $\mathcal{E}(\Phi^{\infty})$ must belong to the set of the finite number of critical values in the theorem. □

8 Proof of Theorem 3.3 and Corollary 3.4

For the proof of Theorem 3.3 we regard $A(E)$ as a subset of the set $\tilde{A}(E)$ of all critical points of the functional $f(\Phi, \mathbf{e})$ in section 5 associated with the critical value E. We consider $f(\Phi, \mathbf{e})$ because the Lagrange multiplier $\mathbf{e}$ is a variable of $f(\Phi, \mathbf{e})$, and we do not need additional constraints. The critical points of $f(\Phi, \mathbf{e})$ automatically satisfies $\langle\varphi_i, \varphi_i\rangle = 1,\ i = 1, \ldots, N$. Thus $A(E)$ can be regarded as a subset of $\tilde{A}(E)$ composed of the first components of $(\Phi, \mathbf{e}) \in \tilde{A}(E)$ such that additional constraints $\langle\varphi_i, \varphi_j\rangle = 0,\ i \ne j$ are satisfied, i.e.

$$A(E) = \{\Phi : (\Phi, \mathbf{e}) \in \tilde{A}(E),\ \langle\varphi_i, \varphi_j\rangle = 0,\ i \ne j\}.$$

In the proof of Theorem 3.3 we show that $\tilde{A}(E)$ is a union of finite number of compact real-analytic manifolds. Then the result follows if $\langle\varphi_i, \varphi_j\rangle$ are real-analytic functions with respect to the local coordinates of the manifolds.

Proof of Theorem 3.3. Let $z^0 = [\Phi^0, \mathbf{e}^0]$ be a critical point of f such that $f(\Phi^0) = \mathcal{E}(\Phi^0) = E < J(N-1)$. Then as in the proof of Theorem 7.1 we can prove that there exist an isomorphism $L : \bigoplus_{i=1}^N H^2(\mathbb{R}^3) \to \bigoplus_{i=1}^N L^2(\mathbb{R}^3)$ and a compact operator M such that $F'(\Phi^0, \mathbf{e}^0) = L + M$. By Atkinson's theorem (see e.g. [2]) $F'(\Phi^0, \mathbf{e}^0) = L + M$ is a Fredholm operator. Thus $Z_1 := \mathrm{Ker}\,(L+M)$ is finite dimensional, and there exists a closed subspace Z_2 of Y_1 such that $Y_1 = Z_1 \bigoplus Z_2$ and $L+M$ is an isomorphism of Z_2 onto $\mathrm{Im}\,(L+M)$, where Y_1 is as in section 5. Write $z^0 = [z_1^0, z_2^0],\ z_i \in Z_i\ (i = 1, 2)$. By the implicit function theorem (Lemma 6.2) there exists a neighborhood U_1 of z_1^0 and a neighborhood U_2 of z_2^0 such that there exists a real-analytic function $\omega : U_1 \to U_2$ satisfying the condition that $z = [z_1, z_2] \in U_1 \times U_2$ is a critical point of f if and only if $z_2 = \omega(z_1)$. Since Z_1 is a finite dimensional linear space, we can use the coefficients of z_1 written as a linear combination of the bases in Z_1 as coordinates for the set of critical points near z^0.

Let $\tilde{A}(E)$ be the set of all critical points of f associated with a critical value $E < J(N-1)$. We make a cover of $\tilde{A}(E)$ by open sets $\tilde{A}(E) \cap (U_1 \times U_2)$ as above. On $(\tilde{A}(E) \cap (U_1 \times U_2)) \cap (\tilde{A}(E) \cap (\tilde{U}_1 \times \tilde{U}_2))$ the coordinate transformation is real-analytic. On each connected component, U_1 has the same dimension. $\tilde{A}(E)$ is sequentially compact. Since Y_1 is a metric space, $\tilde{A}(E)$ is compact. We can take a finite cover from the cover. The set of critical points of $\mathcal{E}(\Phi)$ with the constraints $\langle\varphi_i, \varphi_j\rangle = \delta_{ij},\ 1 \le i, j \le N$ is the set of the first components of the critical points of $f(\Phi, \mathbf{e})$ with the constraints $\langle\varphi_i, \varphi_j\rangle = \delta_{ij},\ i \ne j$. The constraints are written using real-analytic functions on each U_1. Notice that the orbital energy $\mathbf{e}$ is determined by Φ as $\epsilon_i = \langle\varphi_i, \mathcal{F}(\Phi)\varphi_i\rangle$. Thus we can identify Φ with $[\Phi, \mathbf{e}]$. In this way we can see that the set of critical points $A(E)$ of $\mathcal{E}(\Phi)$ is a union of real-analytic subsets of connected components of $\tilde{A}(E)$. □

Proof of Corollary 3.4. We shall prove the first statement by contradiction. Let us assume there exists $\delta > 0$ such that for any finite-dimensional subspace X of $\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$ there exists $\Phi \in A(E)$ satisfying $\|P_{X^\perp}\Phi\| \ge \delta$, contrary to the statement. If this is true, then we can make a sequence $\Phi^j \in A(E)$ which does not include any converging subsequence as follows. We choose arbitrary $\Phi^1 \in A(E)$. Assume we have already chosen $\Phi^1, \ldots, \Phi^k$. Let $\Phi^{k+1} \in A(E)$ be an arbitrary element such that $\|P_{\mathcal{L}(\Phi^1,\ldots,\Phi^k)^\perp}\Phi^{k+1}\| \ge \delta$, where $\mathcal{L}(\Phi^1, \ldots, \Phi^k)$ is the subspace spanned by $\Phi^1, \ldots, \Phi^k$. Such Φ^{k+1} exists by the assumption. Then this sequence satisfies $\|\Phi^i - \Phi^j\| \ge \delta$, for any $i \ne j$. Thus there is no converging subsequence of $\{\Phi^j\}$. This contradicts the compactness of $A(E)$ which follows from Lemma 4.7.

In order to prove the second statement we first show that any tangent vector of $\tilde{A}(E)$ mapped into $\bigoplus_{i=1}^N H^2(\mathbb{R}^3) \oplus \mathbb{R}^N$ by the injection has a nonzero $\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$ component. Let $c(t),\ -1 < t < 1$ be a curve in $\tilde{A}(E)$ which gives a nonzero tangent vector at $c(0) = x^0 \in \tilde{A}(E)$. By the injection j, $c(t)$ is mapped into a curve $j(c(t)) = [\Phi(t), \mathbf{e}(t)],\ -1 < t < 1$ in $\bigoplus_{i=1}^N H^2(\mathbb{R}^3) \oplus \mathbb{R}^N$. Here using HF equation we note $\epsilon_i(t) = \langle \varphi_i(t), \mathcal{F}(\Phi(t))\varphi_i(t)\rangle,\ i = 1, \ldots, N$, where $\mathbf{e}(t) = (\epsilon_1(t), \ldots, \epsilon_N(t))$ and $\Phi(t) = {}^t(\varphi_1(t), \ldots, \varphi_N(t))$. Thus if $\frac{d\varphi_i(0)}{dt} = 0,\ i = 1, \ldots, N$, then $\frac{d\epsilon_i(0)}{dt} = 0,\ i = 1, \ldots, N$. Thus $j_*(c'(0)) = 0$. Since the local coordinates of $\tilde{A}(E)$ is the coefficients of a linear combination in a finite-dimensional subspace Z_1 of $\bigoplus_{i=1}^N H^2(\mathbb{R}^3) \oplus \mathbb{R}^N$, components in Z_1 of $j_*(c'(0))$ is not 0, which contradicts $j_*(c'(0)) = 0$. Thus for any $x^0 \in \tilde{A}(E)$ there exists an open neighborhood U_{x^0} of x^0 such that any tangent vector at any point in U_{x^0} is mapped by j_* to a vector which has a nonzero component in a finite-dimensional subspace Y_{x^0} of $\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$. Thus the restriction of $P_{Y_{x^0}} \circ j_1$ to U_{x^0} is an imbedding of U_{x^0} into Y_{x^0}, where $j_1(p)$ is the Φ component of $j(p)$. Since $\tilde{A}(E)$ is a compact set, $\tilde{A}(E)$ is covered by a finite number of such neighborhoods of a finite number of points $x_1, \ldots, x_m$. Let X_δ be a subspace containing $\bigcup_{i=1}^m Y_{x_i}$. Then clearly $P_{X_\delta}\tilde{A}(E)$ is an imbedding of $\tilde{A}(E)$ into X_δ, where we regarded $\tilde{A}(E)$ as a subset of $\bigoplus_{i=1}^N H^2(\mathbb{R}^3)$ removing components $\mathbf{e}$ determined by $\epsilon_i = \langle \varphi_i, \mathcal{F}(\Phi)\varphi_i\rangle$ from components Φ.

□

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