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Maximum Ionization in Restricted and Unrestricted Hartree-Fock Theory

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Abstract: In this paper, we investigate the maximum number of electrons that can be bound to a system of nuclei modelled by Hartree-Fock theory. We consider both the Restricted and Unrestricted Hartree-Fock models. We are taking a non-existence approach (necessary but not sufficient), in other words we are finding an upper bound on the maximum number of electrons. In giving a detailed account of the proof of Lieb's bound [Theorem 1, Phys. Rev. A 29 (1984), 3018] for the Hartree-Fock models we establish several new auxiliary results, furthermore we propose a condition that, if satisfied, will give an improved upper bound on the maximum number of electrons within the Restricted Hartree-Fock model. For two-electron atoms we show that the latter condition holds.

Keywords: ionization; anions; Hartree-Fock theory

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1. Introduction

Quantum chemistry, the application of quantum mechanics to chemical systems, is used to understand stability, reactivity, and chemical/physical processes at the molecular level by solving the Schrödinger equation (SE). However, the full many-body Schrödinger equation is in general not solvable, and so the goal has been to develop approximate solutions of the many-body SE by developing models capable of explaining experimental data whilst being solved within a reasonable time frame. Two important classes of model are wave-function based models founded on Hartree-Fock (HF) theory and Density Functional Theory (DFT) models.

In Hartree-Fock theory, the N-electron wave function from the Schrödinger equation is approximated by an anti-symmetrized product of N single-electron wave functions (written as a Slater determinant) and the two-electron repulsion operator in the Hamiltonian is replaced by an effective one-electron operator which takes a mean field approach to electron-electron repulsion. Fermi electron correlation is accounted for in Hartree-Fock theory but the Coulomb correlation is missing. Various increasingly sophisticated methods of including the correlated motion of electrons are built upon the HF model, using the HF wavefunction as a reference function either in a perturbation treatment or to systematically select excited state determinants to include in a correlated wave function.

The premise of the second class of models, the DFT models, is to set the Schrödinger equation in terms of electron density, thereby essentially simplifying an N variable problem down to one variable. Although DFT is exact in principle the functional connecting the electron density with the ground state energy remains elusive. Kohn and Sham [1] were able to provide a practical way forward by writing equations analogous to the conventional Hartree-Fock equations. The Kohn-Sham equations use the expression for the HF kinetic

energy to obtain the exact KE of the non-interacting reference system with the same density as the real interacting system. They were able to show that despite working with an orbital model and a single determinant wavefunction for a model system of non-interacting electrons they were still able to incorporate electron correlation. However, the exchange correlation (XC) functional that appears in Kohn-Sham DFT is unknown, and must be chosen in some way. Indeed, choosing a good "guess" for the XC functional is one of the key challenges of DFT.

Thus, HF theory is the bedrock of modern quantum chemistry, and a good understanding of electron correlation, defined as the difference between the exact non-relativistic energy and the HF energy [2], is invaluable for the design and assessment of new models. For these reasons, it is important to understand the interaction of electrons within the HF model, in particular within anions, as it is known that electron correlation plays a crucial role in their stability.

However, even for the simplest two-electron system, the hydride ion, there remains unanswered questions regarding its stability at the Hartree-Fock level of theory, and this is the motivation for this paper. A recent review by the authors [3] detailed existing numerical/computational and theoretical works on the bound state stability of the hydride ion, where the term bound state refers to the existence of a discrete eigenvalue below the lowest continuum threshold. Numerical calculations and mathematical proofs agree that the many-body, non-relativistic, time-independent Schrödinger equation for the hydride ion supports a single bound state. However, no such result has been reported for the Hartree-Fock hydride ion.

For the HF model, Lieb and Simon in [4] showed that if

$$Z \geq N, \tag{1}$$

a ground state (i.e., a minimizer for the HF energy functional) exists. However for the H^- case, where $Z = 1$ and $N = 2$, this does not help. In [5] Lions gave a new proof of existence, and, furthermore, he showed that the N components of the ground state (the minimizing orbitals) correspond to eigenfunctions associated with the lowest N eigenvalues of the so-called Fock operator; recall that the Euler-Lagrange equations corresponding to the HF model are called HF equations and they can be formulated by means of a mean-field operator, the Fock operator. However, Lions too did not improve on the bound $Z \geq N$. Hantsch in [6] showed, for Restricted Hartree-Fock (RHF) theory, that minimizers exist for $Z \geq N - 1$, which in particular shows that a minimizer exists for the hydride atom H^- for RHF theory. However, unlike Lieb and Simon, and Lions, Hantsch did not show that the minimizing orbitals are eigenfunctions associated with the N lowest eigenvalues of the Fock operator.

The fundamental question "How many electrons can a nucleus bind?" was first addressed rigorously by Ruskai [7] and Sigal [8]. Mathematically, the question amounts to finding the maximal number $N_{\max}$ of electrons such that for an atomic system with a static nucleus of charge $Z > 0$ modelled by the atomic Schrödinger operator $H_N(Z)$, the ground state energy $E_N(Z) = \inf \operatorname{spec}(H_N(Z))$ remains below the essential spectrum of $H_N(Z)$. Experimental and numerical evidence [9,10] suggests that

$$N_{\max} < Z + 2 \tag{2}$$

for all Z associated with the elements of nature but this "ionization conjecture" has not yet been established; however for the specific case of the atomic RHF model, Theorem 2 below establishes the criteria for it to hold. Zhislin [11] derived a lower bound of the form $N_{\max} \geq Z$. Ruskai [7,12] and Sigal [8] showed an upper bound for $N_{\max}$, specifically for fermions, Ruskai achieved

$$N_{\max} \leq CZ^{6/5}. \tag{3}$$

This quite generous bound was improved on in Lieb's 1984 paper [13]. In this paper, Lieb shows that for a general molecule with K nuclei and total charge Z,

$$N_{\max} < 2Z + K. \tag{4}$$

For the hydrogen nucleus, $Z = 1$ and $K = 1$, this indicates that H^- is the only stable hydride ion. However, for larger Z, Lieb's result is still not as strong as one could wish. Nam [14] improved Lieb's bound for larger Z, namely

$$N_{\max} < 1.22Z + 3Z^{1/3}. \tag{5}$$

For the HF model, Solovej [15] proved that

$$N_{\max} < Z + Q. \tag{6}$$

Both Nam's bound and Solovej's bound, however still fall short of the expected ionization conjecture; although Solovej managed to obtain the factor 1 in front of Z, the constant Q was not provided (or estimated).

In the present work, we return to the bound provided by Lieb [13] on the maximum negative ionization (4). This is a necessary condition for non-existence but it is not sufficient to guarantee the existence of a bound state for systems that do satisfy (4). Thus, although the hydride ion satisfies (4), and in the case of the many-body SE the bound state stability of H^- has been rigorously proven [16], in the case of HF theory a bound state is not excluded but also not proven to exist. In [13] the primary focus was on the many-body case but Lieb provided a tantalising outline of how to extend his result to the unrestricted Hartree-Fock method. Within HF theory there are three main models—general Hartree-Fock (GHF) where the basis spin orbitals may be mixtures of functions having α and β spins, unrestricted Hartree-Fock (UHF) where each spin orbital is a product spin orbital of a spatial wavefunction and a spin function (α or β), and restricted Hartree-Fock (RHF) where for a closed-shell system each spatial wave function holds two electrons, one of α spin and the other of β spin. In conventional quantum chemistry methods, Slater determinants are comprised of product spin orbitals and the spatial functions are taken to be real.

In this paper, the mathematical proof of the Lieb criterion is extended to explicitly consider product spin orbitals with real basis functions within the restricted and unrestricted HF formalisms to mirror the details used in conventional HF numerical calculations. It is shown that (4) holds for all these HF scenarios, and a stronger condition for atoms within RHF is presented.

This paper is structured as follows—we start by presenting the main results and several auxiliary results in Sections 2 and 3. Sections 4 and 5 define the quantum system and the HF models. As applications of the auxiliary results, we provide the proof of Theorem 1 for these Hartree-Fock methods in Sections 6–8, firstly for the atomic RHF case, then for the molecular RHF case, and finally for the molecular UHF case. The proof of Theorem 2 is given in Section 9 and the proofs of the auxiliary results are provided in the Appendix A.

2. Results

In [13] Lieb claims that the repulsion term is given by

$$R = \frac{1}{2}N(N-1)\int_{\mathbb{R}^{3N}} |\psi(X)|^2 |x_1 - x_2|^{-1} [\phi(x_1)^{-1} + \phi(x_2)^{-1}] d^{3N}X, \tag{7}$$

where $X = x_1, \ldots, x_N$ is on $\mathbb{R}^{3N}$, x_i denotes the $\mathbb{R}^3$ coordinates of the ith electron, ψ is the full wave funtion, and $\phi(\cdot)$ is a positive function. However, here we start with R being equal to

$$R = \left(\frac{1}{2}N(N-1) - N_\alpha N_\beta\right)\sum_\sigma \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \frac{\phi(x_1)^{-1}+\phi(x_2)^{-1}}{|x_1-x_2|} d^{3N}X + \sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\phi(x)^{-1}+\phi(y)^{-1}}{|x-y|}|\psi_i^\alpha(x)|^2|\psi_j^\beta(y)|^2 dxdy, \quad (8)$$

where σ is the spin coordinate, N_α and N_β are the number of spin up and spin down electrons, respectively, and x, y are the coordinates of an electron of spin α or β respectively.

While (7) turns out to be true, we found that it is non-trivial, especially when one considers the molecular UHF case. In this paper, we fill in the details of Lieb's proof outline, and in particular we need the following key new result:

Lemma 1. *Consider the UHF model with N_α terms of spin $+$ and N_β terms of spin $-$. Let $\sigma = \{\sigma_1, \ldots, \sigma_N\}$ be chosen so that the spin terms of the corresponding single-particle wave functions will be non-trivial.*

Let us assume that ϕ_p corresponds to a positive spin single wave function and ϕ_q will correspondingly be a negative spin single wave function. Then,

$$\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_p, x_q)\, dX = \frac{(N_\alpha-1)!(N_\beta-1)!}{N!}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3} F(x,y)|\phi_i^\alpha(x)|^2|\phi_j^\beta(y)|^2\, dx\, dy. \quad (9)$$

Using this lemma, we are able to give a detailed proof of Lieb's theorem (see Theorem 1 of [13]):

Theorem 1. *Suppose we are using either the molecular Restricted Hartree-Fock model or the molecular Unrestricted Hartree-Fock model. Let N be the number of electrons in the system, Z the total charge of the system, and K the number of positively charged (fixed) particles. If the system is stable, it must satisfy*

$$N < 2Z + K. \quad (10)$$

In particular for the atomic case, we shall have $K = 1$ and thus the result becomes

$$N < 2Z + 1. \quad (11)$$

By imposing an additional assumption on our wave functions, we can achieve the desired bound (2):

Theorem 2. *For the atomic Restricted Hartree-Fock theory, let N be the number of electrons in the system and Z the charge of the nucleus. Suppose that the single particle wave functions satisfy*

$$\sum_{i=1}^{p}\int_{\mathbb{R}^3}|x|u_i(x)(-\Delta u_i(x))dx + 3\sum_{i=1}^{p}\sum_{j=1}^{p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|x|\frac{\overline{u_i(x)}u_i(x')u_j(x)\overline{u_j(x')}}{|x-x'|}dxdx' - 2\sum_{i=1}^{p}\sum_{j=1}^{p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|x|\frac{|u_i(x)|^2|u_j(x')|^2}{|x-x'|}dxdx' \geq 0, \quad (12)$$

where $p = N/2$, u_i are the single particle wave function, and multiplying (12) by 2 corresponds to $\widetilde{T} + 3\widetilde{K} - \widetilde{U}$, where $\widetilde{T}$, $\widetilde{K}$ and $\widetilde{U}$ are defined in Equations (54) to (59). Then

$$N < Z + 2. \quad (13)$$

The physical interpretation of (12) is unclear but, interestingly, for $p = 1$ (i.e., for two electrons) it holds; see Remark 1 for details. Whether it holds for $p > 1$ is under investigation. We also note that this is a non-existence theorem (necessary but not sufficient) in the same way as Theorem 1 of [13] is, and so although the hydride ion satisfies Equation (13) it does not guarantee that the system holds a bound state (and all numerical calculations indicate it does not [3]).

3. Auxiliary Results

For our proofs of the main theorem, we will need to find a way to write the Coulomb parts in terms of the wave function. This is our motivation for Lemma 2, which lets us write the weighted integral of the wave function in terms of single particle wave functions. As a corollary to Lemma 2, we have Corollary 2, which considers the wave function summed over all possible spins. To the best of our knowledge these results are new. We provide the lengthy proofs in the Appendix A.

Lemma 2. *Let N be the number of electrons and let $F : \mathbb{R}^3 \times \mathbb{R}^3 \to \mathbb{R}$ be a smooth function. Also let $\sigma = \{\sigma_1, \ldots, \sigma_N\}$ be chosen so that the spin term of the corresponding single-particle wave functions will be non-trivial. If ψ is a stable solution for the RHF model, then there exists an $\widetilde{N}$ depending only on N so that*

$$\begin{aligned} &\widetilde{N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2) dX \\ &= \sum_{1\le i<j\le p} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x,y)\left(|\phi_i|^2|\phi_j(y)|^2 - \overline{\phi_i(x)}\phi_j(x)\phi_i(y)\overline{\phi_j(y)}\right) dxdy. \end{aligned} \tag{14}$$

Similarly, if ψ is a stable solution for the UHF model, then there exists $\widetilde{N}_1$ and $\widetilde{N}_2$ (depending only on N) so that

$$\begin{aligned} &\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2) dX \\ =&\widetilde{N}_1 \sum_{1\le i<j\le N_\alpha} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x,y)\left(|\phi_i^\alpha(x)|^2|\phi_j^\alpha(y)|^2 - \overline{\phi_i^\alpha(x)}\phi_j^\alpha(x)\phi_i^\alpha(y)\overline{\phi_j^\alpha(y)}\right) dxdy \\ &+ \widetilde{N}_2 \sum_{1\le i<j\le N_\beta} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x,y)\left(|\phi_i^\beta(x)|^2|\phi_j^\beta(y)|^2 - \overline{\phi_i^\beta(x)}\phi_j^\beta(x)\phi_i^\beta(y)\overline{\phi_j^\beta(y)}\right) dxdy. \end{aligned} \tag{15}$$

We also have the following result.

Corollary 1. *Let N be the number of electrons, and let $F : \mathbb{R}^3 \times \mathbb{R}^3 \to \mathbb{R}$ be a smooth function.*

1. *If ψ is a stable solution for the RHF model, then*

$$\begin{aligned} &\sum_{\sigma\in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)\, dX \\ =&\frac{2}{p(p-1)} \sum_{1\le i<j\le p} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x,y)\left(|\phi_i(x)|^2|\phi_j(y)|^2 - \overline{\phi_i(x)}\phi_j(x)\phi_i(y)\overline{\phi_j(y)}\right) dxdy. \end{aligned} \tag{16}$$

2. *If ψ is a stable solution for the UHF model with N_α positive spin electrons and N_β negative spin electrons, then*

$$\begin{aligned}&\left(\frac{1}{2}N(N-1)-N_\alpha N_\beta\right)\sum_{\sigma\in S^N}\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2F(x_1,x_2)\,dX\\&=\sum_{i<j}^{N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(x,y)\left(|\phi_i^\alpha(x)|^2|\phi_j^\alpha(y)|^2-\overline{\phi_i^\alpha(x)}\phi_j^\alpha(x)\phi_j^\alpha(y)\overline{\phi_i^\alpha(y)}\right)dxdy\\&+\sum_{i<j}^{N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(x,y)\left(|\phi_i^\beta(x)|^2|\phi_j^\beta(y)|^2-\overline{\phi_i^\beta(x)}\phi_j^\beta(x)\phi_j^\beta(y)\overline{\phi_i^\beta(y)}\right)dxdy.\end{aligned}\tag{17}$$

However, these results are not quite sufficient for proving the molecular UHF case, for which we will need Lemma 1 (see Section 2) and its Corollary 2; achieved by summing over the spin terms.

Corollary 2. *Consider the UHF model with N_α terms of spin $+$ and N_β terms of spin $-$. Let us assume that $p\le N_\alpha$ and $q>N_\alpha$, so ϕ_p will be a positive spin single wave function and ϕ_q will correspondingly be a negative spin single wave function. Then,*

$$\begin{aligned}&\sum_{\sigma\in S^N}\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2F(x_p,x_q)\,dX\\&=\frac{1}{N_\alpha N_\beta}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}F(x,y)|\phi_i^\alpha(x)|^2|\phi_j^\beta(y)|^2\,dx\,dy.\end{aligned}\tag{18}$$

The above lemmas, Lemma 1 and their corollaries will be proven in the Appendix A, together with the following lemma, which is a modification of Lemma 1 of [13]:

Lemma 3. *For a function f defined on $\mathbb{R}^3$ so that $f(x_i)\psi(X)\in L^2(\mathbb{R}^{3N})$ with $x_i\in\mathbb{R}^3$ for any $i=1,\dots,N$, we have*

$$\begin{aligned}\mathrm{Re}\int_{\mathbb{R}^{3N}}|\psi(X)|^2\sum_{1\le i<j\le p}f(x_i)f(x_j)dX\ge&\frac{1}{2}\left|\int_{\mathbb{R}^{3N}}|\psi(X)|^2\sum_{i=1}^{p}f(x_i)\right|^2\\&-\frac{1}{2}\int_{\mathbb{R}^{3N}}|\psi(X)|^2\sum_{i=1}^{p}f(x_i)^2dX.\end{aligned}\tag{19}$$

As usual, Re *means the real part of a number.*

4. Preliminaries

We consider the N-electron quantum system described by the Schrödinger Hamiltonian

$$H_N(X)=-\sum_{i=1}^{N}\Delta_i+\sum_{i=1}^{N}V(x_i)+\sum_{1\le i<j\le N}\frac{1}{|x_i-x_j|},\tag{20}$$

where for $1\le i\le N$, we have $x_i\in\mathbb{R}^3$, and $X=(x_1,\dots,x_N)\in\mathbb{R}^{3N}$. By Δ_i, we mean

$$\Delta_i=\sum_{j=1}^{3}\frac{\partial^2}{\partial x_{i,j}^2},\tag{21}$$

with $x_{i,j}\in\mathbb{R}$ being the jth element of $x_i\in\mathbb{R}^3$. The potential is given by

$$V(x)=-\sum_{s=1}^{K}\frac{Z_s}{|x-R_s|}.\tag{22}$$

The potential describes K positively charged static nuclei with charges $Z_s \in \mathbb{R}^+$ at positions $R_s \in \mathbb{R}^3$, for $s \in \{1, \ldots, K\}$. Related to this we define the total charge of the system to be

$$Z = \sum_{s=1}^{K} Z_s. \tag{23}$$

We will be considering Hartree-Fock theory with spin, so this Hamiltonian will act on wave functions $\psi \in L^2_{S^N}(\mathbb{R}^{3N})$ that can be written in the form

$$\psi(x_1, \sigma_1, \ldots, x_N, \sigma_N) = \frac{1}{\sqrt{N!}} \det u_i(x_j, \sigma_j), \tag{24}$$

where $(x_1, \ldots, x_N) \in \mathbb{R}^{3N}$. Correspondingly, we write $\sigma = (\sigma_1, \ldots, \sigma_N) \in S^N$, where $S = \{+, -\}$. We have that $L^2_{S^N}$ is the space of L^2 functions on $\mathbb{R}^{3N}$ that also have N spin terms. We have that $u_i \in H^1(\mathbb{R}^3; \mathbb{C}^2)$; here we retain the use of the complex conjugate but the analysis applies to complex valued or real-valued u_i. For our particular models,

$$\langle u_i, u_j \rangle := \sum_{\sigma \in S} \int_{\mathbb{R}^3} \overline{u_i(x, \sigma)} u_j(x, \sigma) dx = \delta_{i,j}, \tag{25}$$

where $\delta_{i,j}$ is the usual Kronecker delta. Functions that take the form in (24) are known as Slater determinants, the u_i are known as single-particle wave functions. One of the main features is that wave functions ψ of this form are anti-symmetric, and hence $|\psi|^2$ will be symmetric.

The fully correlated ground state energy is given by

$$E_N = \inf_{\|\psi\|=1} \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} \overline{\psi(X, \sigma)} H_N(X) \psi(X, \sigma) dX = \inf_{\|\psi\|=1} \langle \psi, H_N \psi \rangle, \tag{26}$$

where

$$\|\psi\|^2 = \langle \psi, \psi \rangle = \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} \overline{\psi(X, \sigma)} \psi(X, \sigma) \, dX, \tag{27}$$

and we minimize over $\psi \in L^2_{S^N}$ that are of the form given in Equation (24).

As in [17] we shall also define the single-particle density corresponding to a wave function ψ by

$$\begin{aligned} \rho(x) &= N \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3(N-1)}} |\psi(x, \sigma_1, x_2, \sigma_2, \ldots, x_N, \sigma_N)|^2 dx_2 \ldots dx_N \\ &= N \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3(N-1)}} |\psi(X, \sigma)|^2 dX_i, \quad i \geq 2. \end{aligned} \tag{28}$$

The second line introduces the short-hand notation, $X := (x_1, \ldots, x_N)$ and $dX_i = dx_1, \ldots dx_{i-1} dx_{i+1} \ldots dx_N$. Note also that we are summing over all the possible σ.

For functions that are Slater determinants, we can write the density as

$$\rho(x) = \sum_{\sigma} \sum_{i=1}^{N} |u_i(x, \sigma)|^2. \tag{29}$$

For our work we shall, as in Lieb and Simon [4], write the system in (26) as N coupled Euler-Lagrange equations. For $i \in \{1, \ldots, N\}$, we have

$$h u_i = \epsilon_i u_i, \tag{30}$$

where ϵ_i are the Lagrange multipliers, and the single-particle operator h is given by

$$(hw)(x) = -\Delta w(x) + V(x)w(x) + U_\psi(x)w(x) - \big(K_\psi w\big)(x), \tag{31}$$

where V is given in (22) and

$$U_\psi(x) = \sum_{\sigma\in S^N}\sum_{j=1}^{N}\int_{\mathbb{R}^3}|x-y|^{-1}|u_j(y,\sigma)|^2dy, \tag{32}$$

$$\big(K_\psi w\big)(x) = \sum_{\sigma\in S^N}\sum_{j=1}^{N}u_j(x)\int_{\mathbb{R}^3}|x-y|^{-1}\overline{u_j(y,\sigma)}w(y,\sigma)dy. \tag{33}$$

We call $(-\Delta)$ the kinetic energy term, V the nucleus-electron term, U_ψ the direct (Coulomb) term, and K_ψ the exchange term. With a slight abuse of notation, we write the single-particle operator h as

$$h = T + V + U - K. \tag{34}$$

Depending on whether we are using the Restricted Hartree-Fock model or the Unrestricted Hartree-Fock model, these terms will look different.

5. Restricted Hartree-Fock and Unrestricted Hartree-Fock

In the Restricted Hartree-Fock (RHF) model, we only consider systems with an even number of electrons, in particular we have p pairs of electrons, so $N = 2p$. In this model, each pair shares the spatial wave function, but has the opposite spin. In other words, the Slater determinant is made of p pairs of wave functions of the form

$$\{\phi_i(x)\alpha(\sigma), \phi_i(x)\beta(\sigma)\}_{1\le i\le p}, \tag{35}$$

where we define

$$\alpha(\sigma) = \begin{cases} 1, & \sigma = + \\ 0, & \sigma = - \end{cases} \tag{36}$$

and

$$\beta(\sigma) = \begin{cases} 0, & \sigma = + \\ 1, & \sigma = - \end{cases} \tag{37}$$

and we require that

$$\sum_{\sigma\in S}\int_{\mathbb{R}^3}\overline{u_i(x,\sigma)}u_j(x,\sigma)dx = \delta_{i,j}, \tag{38}$$

where

$$u_j(x,\sigma) = \begin{cases} \phi_j(x)\alpha(\sigma), & j \le p, \\ \phi_{j-p}(x)\beta(\sigma), & j > p. \end{cases} \tag{39}$$

If we choose $i, j \le p$, the Kronecker delta condition implies that

$$\begin{aligned} \delta_{i,j} &= \int_{\mathbb{R}^3}\overline{\phi_i(x)\sigma(+)}\phi_j(x)\sigma(+)dx \\ &\quad + \int_{\mathbb{R}^3}\overline{\phi_i(x)\sigma(-)}\phi_j(x)\sigma(-)dx \\ &= \int_{\mathbb{R}^3}\overline{\phi_i(x)}\phi_j(x)dx. \end{aligned} \tag{40}$$

For the Unrestricted Hartree-Fock (UHF) model, the single-particle wave functions are of the form

$$\{\phi_1^\alpha\alpha, \ldots, \phi_{N_\alpha}^\alpha\alpha; \phi_1^\beta, \ldots, \phi_{N_\beta}^\beta\beta\}, \tag{41}$$

where the integers $N_\alpha + N_\beta = N$. In particular, we can note that the Restricted Hartree-Fock model is a special case of the Unrestricted Hartree-Fock model, where $N_\alpha = p = N_\beta$, and for all i we have $\phi_i^\alpha = \phi_i^\beta$.

As in the case of the Restricted Hartree-Fock, considering the Kronecker delta condition for the Unrestricted Hartree-Fock case for the positive spin terms will give for $i, j \leq N_\alpha$ that

$$\delta_{i,j} = \int_{\mathbb{R}^3} \overline{\phi_i^\alpha(x)} \phi_j^\alpha(x) dx, \tag{42}$$

and for the negative spin case it will be

$$\delta_{i,j} = \int_{\mathbb{R}^3} \overline{\phi_i^\beta(x)} \phi_j^\beta(x) dx \tag{43}$$

for $i, j \leq N_\beta$.

The outline of our argument is as follows. We multiply the Euler-Lagrange equations with the spacial wave function u_i and a weight function w, we integrate over the $\mathbb{R}^3$ space and the spin space, then finally sum over the N spacial wave functions. In other words, we will have

$$\sum_{\sigma \in S} \sum_{i=1}^{N} \int_{\mathbb{R}^3} \overline{w(x) u_i(x)} (h u_i)(x)\, dx. \tag{44}$$

Let us focus on the terms that come from the Direct Coulomb operator, which relates to U_ψ, and the Exchange operator, which relates to K_ψ. The term involving the Direct Coulomb term is given by

$$\begin{aligned}
&\sum_{\sigma \in S} \sum_{i=1}^{N} \int_{\mathbb{R}^3} \overline{w(x)} |u_i(x,\sigma)|^2 U_\psi(x,\sigma)\, dx \\
&= \sum_{\sigma \in S} \sum_{i=1}^{N} \int_{\mathbb{R}^3} \overline{w(x)} |u_i(x,\sigma)|^2 \sum_{j=1}^{N} \sum_{\sigma' \in S} \int_{\mathbb{R}^3} |x-y|^{-1} |u_j(y,\sigma')|^2\, dy dx \\
&= \sum_{\sigma \in S} \sum_{\sigma' \in S} \sum_{i=1}^{N} \sum_{j=1}^{N} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\overline{w(x)}}{|x-y|} |u_i(x,\sigma)|^2 |u_j(y,\sigma')|^2\, dy dx.
\end{aligned} \tag{45}$$

Recalling that $\alpha(-) = 0 = \beta(+)$, we have for the UHF case that

$$\begin{aligned}
&\sum_{\sigma \in S} \sum_{\sigma' \in S} \sum_{i=1}^{N} \sum_{j=1}^{N} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\overline{w(x)}}{|x-y|} |u_i(x,\sigma)|^2 |u_j(y,\sigma')|^2 dy dx \\
&= \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\alpha} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\overline{w(x)}}{|x-y|} |\phi_i^\alpha(x)|^2 |\phi_j^\alpha(y)|^2 dy dx \\
&+ \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\overline{w(x)}}{|x-y|} |\phi_i^\alpha(x)|^2 |\phi_j^\beta(y)|^2 dy dx \\
&+ \sum_{i=1}^{N_\beta} \sum_{j=1}^{N_\alpha} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\overline{w(x)}}{|x-y|} |\phi_i^\beta(x)|^2 |\phi_j^\alpha(y)|^2 dy dx \\
&+ \sum_{i=1}^{N_\beta} \sum_{j=1}^{N_\beta} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\overline{w(x)}}{|x-y|} |\phi_i^\beta(x)|^2 |\phi_j^\beta(y)|^2 dy dx.
\end{aligned} \tag{46}$$

If we consider the special case of the RHF model, we immediately see that each term on the right-hand side of (46) is the same, and we have

$$\sum_{\sigma\in S}\sum_{i=1}^{N}\int_{\mathbb{R}^3}\overline{w}u_i U_\psi u_i dx = 4\sum_{i=1}^{p}\sum_{j=1}^{p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\overline{w(x)}}{|x-y|}|\phi(x)|^2|\phi(y)|^2 dydx. \tag{47}$$

We next consider the term involving the Exchange operator. We have for the UHF that

$$\begin{aligned}
&\sum_{\sigma\in S}\sum_{i=1}^{N}\int_{\mathbb{R}^3}\overline{wu_i}K_\psi u_i dx = \sum_{\sigma\in S}\sum_{i=1}^{N}\int_{\mathbb{R}^3}\overline{w(x)u_i(x,\sigma)}\left(K_\psi u_i\right)(x,\sigma)dx\\
&=\sum_{\sigma\in S}\sum_{i=1}^{N}\int_{\mathbb{R}^3}\overline{w(x)u_i(x,\sigma)}\\
&\left(\sum_{\sigma'\in S}\sum_{j=1}^{N}u_j(x,\sigma)\int_{\mathbb{R}^3}|x-y|^{-1}\overline{u_j(y,\sigma')}u_i(y,\sigma')dy\right)dx\\
&=\sum_{\sigma\in S}\sum_{\sigma'\in S}\sum_{i=1}^{N}\sum_{j=1}^{N}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\overline{w(x)}}{|x-y|}\left(\overline{u_i(x,\sigma)}u_i(y,\sigma')u_j(x,\sigma)\overline{u_j(y,\sigma')}\right)dydx.
\end{aligned}\tag{48}$$

Because $\alpha(+)\alpha(-)=0$, it follows that the non-zero terms will have $\sigma=\sigma'$. Hence, for the UHF model we have

$$\begin{aligned}
\sum_{\sigma\in S}\sum_{i=1}^{N}\int_{\mathbb{R}^3}\overline{w}u_i K_\psi u_i dx &= \sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\overline{w(x)}}{|x-y|}\overline{\phi_i^\alpha(x)}\phi_i^\alpha(y)\phi_j^\alpha(x)\overline{\phi_j^\alpha(y)}dydx\\
&+\sum_{i=1}^{N_\beta}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\overline{w(x)}}{|x-y|}\overline{\phi_i^\beta(x)}\phi_i^\beta(y)\phi_j^\beta(x)\overline{\phi_j^\beta(y)}dydx.
\end{aligned}\tag{49}$$

For the special case of RHF, the term involving the Exchange operator becomes

$$\sum_{\sigma\in S}\sum_{i=1}^{N}\int_{\mathbb{R}^3}\overline{w}u_i K_\psi u_i dx = 2\sum_{i=1}^{p}\sum_{j=1}^{p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\overline{w(x)}}{|x-y|}\overline{\phi_i(x)}\phi_i(y)\phi_j(x)\overline{\phi_j(y)}dydx. \tag{50}$$

6. Proof of Theorem 1 for the Atomic RHF Model

We first prove Theorem 1 for the atomic RHF model. Hence we have that

$$V(x) = -\frac{Z}{|x|}. \tag{51}$$

We start with Equation (30). We multiply both sides by $|x|u_i(x)\neq 0$, we integrate over $\mathbb{R}^3$ and sum over spin, then we sum over N. This gives us

$$\sum_{i=1}^{N}\sum_{\sigma\in S}\int_{\mathbb{R}^3}|x|\overline{u_i(x,\sigma)}hu_i(x,\sigma)\,dx = \sum_{\sigma}\sum_{i=1}^{N}\epsilon_i\int_{\mathbb{R}^3}|x||u_i(x,\sigma)|^2dx := \widetilde{E}. \tag{52}$$

As shown in [17], each $\epsilon_i\leq 0$, and hence $\widetilde{E}$ in (52) is non-positive. The left-hand side of (52) is

$$\begin{aligned}
&\sum_{\sigma\in S}\sum_{i=1}^{N}\int_{\mathbb{R}^3}|x|\overline{u_i(x,\sigma)}(-\Delta)u_i(x,\sigma)dx+\sum_{\sigma\in S}\sum_{i=1}^{N}\int_{\mathbb{R}^3}V(x)|x||u_i(x,\sigma)|^2dx\\
&+\sum_{\sigma\in S}\sum_{i=1}^{N}\int_{\mathbb{R}^3}U_\psi(x,\sigma)|x||u_i(x,\sigma)|^2dx-\sum_{\sigma\in S}\sum_{i=1}^{N}\int_{\mathbb{R}^3}|x|\overline{u_i(x,\sigma)}K_\psi(u_i(x,\sigma))dx\\
&=:\widetilde{T}+\widetilde{V}+\widetilde{U}-\widetilde{K}.
\end{aligned}\tag{53}$$

We shall now write these out as terms of the RHF model. The term involving the kinetic energy operator becomes

$$\widetilde{T} = 2\sum_{i=1}^{p}\int_{\mathbb{R}^3} |x|\overline{u_i(x)}(-\Delta u_i(x))dx. \tag{54}$$

Since

$$\mathrm{Re}\,\langle |x|f, -\Delta f\rangle \geq 0 \tag{55}$$

for all $f \in H^1(\mathbb{R}^3)$ as shown in [13], it follows that

$$\widetilde{T} \geq 0. \tag{56}$$

For the potential term, we use the density in Equations (28) and (29) to write

$$\begin{aligned}\widetilde{V} &= \sum_{\sigma\in S}\sum_{i=1}^{N}\int_{\mathbb{R}^3} V(x)|x||u_i(x,\sigma)|^2dx \\ &= -\int_{\mathbb{R}^3} Z\rho(x)dx = -ZN\sum_{\sigma}\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2dX = -ZN.\end{aligned} \tag{57}$$

The term expressed via the direct Coulomb operator is

$$\begin{aligned}\widetilde{U} &= \sum_{\sigma\in S}\sum_{i=1}^{N}\int_{\mathbb{R}^3} U_\psi(x,\sigma)|x||u_i(x,\sigma)|^2dx \\ &= 4\sum_{i=1}^{p}\sum_{j=1}^{p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|x|\frac{|u_i(x)|^2|u_j(x')|^2}{|x-x'|}dxdx'.\end{aligned} \tag{58}$$

The term involving the exchange operator is

$$\widetilde{K} = 2\sum_{i=1}^{p}\sum_{j=1}^{p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|x|\frac{\overline{u_i(x)}u_i(x')u_j(x)\overline{u_j(x')}}{|x-x'|}dxdx'. \tag{59}$$

Since $\widetilde{T}$ is positive, we have

$$0 > \widetilde{T} + \widetilde{V} + \widetilde{U} - \widetilde{K} \geq \widetilde{V} + \widetilde{U} - \widetilde{K} = \widetilde{V} + \frac{1}{2}\widetilde{U} + \frac{1}{2}\left(\widetilde{U} - 2\widetilde{K}\right). \tag{60}$$

For the $\frac{1}{2}\widetilde{U}$ term, we use symmetry and the triangle inequality to write

$$\begin{aligned}\frac{1}{2}\widetilde{U} &= \sum_{i=1}^{p}\sum_{j=1}^{p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{|x|+|y|}{|x-y|}|u_i(x)|^2|u_j(x')|^2dxdx' \\ &\geq \sum_{i=1}^{p}\int_{\mathbb{R}^3}|u_i(x)|^2dx\sum_{j=1}^{p}\int_{\mathbb{R}^3}|u_j(x')|^2dx' = p^2.\end{aligned} \tag{61}$$

For the $\widetilde{U} - 2\widetilde{K}$ term, we use $\sum_{i \neq j} = 2\sum_{i<j}$ to get

$$\begin{aligned}\widetilde{U} - 2\widetilde{K} =& 4\sum_{i=1}^{p}\sum_{j=1}^{p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|x|\frac{|u_i(x)|^2|u_j(x')|^2}{|x-x'|}dxdx' \\ & - 4\sum_{i=1}^{p}\sum_{j=1}^{p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}|x|\frac{\overline{u_i(x)}u_i(x')u_j(x)\overline{u_j(x')}}{|x-x'|}dxdx' \\ =& 8\sum_{i<j}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{|x|}{|x-x'|}\Big(|u_i(x)|^2|u_j(x')|^2 \\ & - \overline{u_i(x)}u_i(x')u_j(x)\overline{u_j(x')}\Big)dxdx'. \end{aligned} \tag{62}$$

We use (16) with

$$F(x,y) = \frac{|x|}{|x-y|} \tag{63}$$

to write

$$\begin{aligned}\widetilde{U} - 2\widetilde{K} &= 8\frac{1}{2}p(p-1)\sum_{\sigma}\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2\frac{|x_1|}{|x_1-x_2|}dX \\ &= 4\frac{1}{2}p(p-1)\sum_{\sigma}\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2\frac{|x_1|+|x_2|}{|x_1-x_2|}dX \\ &= 2p(p-1)\sum_{\sigma}\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2\frac{|x_1|+|x_2|}{|x_1-x_2|}dX. \end{aligned} \tag{64}$$

By the triangle inequality, we have

$$\frac{|x_1|+|x_2|}{|x_1-x_2|} \geq 1, \tag{65}$$

and thus

$$\widetilde{U} - 2\widetilde{K} \geq 2p(p-1). \tag{66}$$

So, if we have a stable solution, it follows that

$$\begin{aligned} 0 &> \widetilde{V} + \frac{1}{2}\widetilde{U} + \frac{1}{2}\Big(\widetilde{U} - 2\widetilde{K}\Big) \\ &\geq -2pZ + p^2 + p(p-1). \end{aligned} \tag{67}$$

In other words,

$$2Z + 1 > 2p, \tag{68}$$

that is,

$$N < 2Z + 1. \tag{69}$$

7. Proof of Theorem 1 for the Molecular RHF Model

Before we start the proof, we introduce some notation. The potential will now be given by

$$V(x) = -\sum_{s=1}^{K} Z_s|x - R_s|^{-1} \tag{70}$$

and we will multiply by a weight function $1/w(x)$, defined so that

$$w(x) = \sum_{s=1}^{K} \mu_s|x - R_s|^{-1}. \tag{71}$$

We also define

$$\gamma_s := \int_{\mathbb{R}^3} \rho(x)|x - R_s|^{-1} w(x)^{-1}, \tag{72}$$

where we recall

$$\rho(x) = N \sum_{\sigma} \int_{\mathbb{R}^{3(N-1)}} |\psi(X,\sigma)|^2 dX_1, \tag{73}$$

and hence

$$\int_{\mathbb{R}^3} \rho(x) dx = N. \tag{74}$$

We can now begin the proof for the molecular RHF model.

As before, the term involving the kinetic energy operator is nonnegative, that is, $\widetilde{T} \geq 0$. The term expressed via the potential term will be of the form

$$\begin{aligned}
\widetilde{V} &= \sum_{\sigma \in S} \sum_{i=1}^{N} \int_{\mathbb{R}^3} |u_i(x,\sigma)|^2 V(x) \frac{1}{w(x)} dx \\
&= \sum_{\sigma \in S} \int_{\mathbb{R}^3} \rho(x) V(x) w(x)^{-1} dx \\
&= -\sum_{s=1}^{K} Z_s \sum_{\sigma \in S} N \int_{R^{3N}} |\psi(X,\sigma)|^2 |x_1 - R_s|^{-1} \frac{1}{w(x_1)} dX \\
&= -\sum_{s=1}^{K} Z_s \gamma_s.
\end{aligned} \tag{75}$$

Following the arguments of the atomic case, we have that the term involving the direct Coulomb energy minus twice the term expressed via the exchange energy is given by

$$\widetilde{U} - 2\widetilde{K} = 2p(p-1) \sum_{\sigma} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \frac{w^{-1}(x_1) + w^{-1}(x_2)}{|x_1 - x_2|} dX. \tag{76}$$

However, $|\psi(x_1, \ldots, x_p)|^2$ is symmetric with respect to x_i and x_j for $i \neq j$. We also recall that for the ordered sum $\sum_{1 \leq i < j \leq p}$ there are $p(p-1)/2$ terms. Therefore, we have that

$$\begin{aligned}
\widetilde{U} - 2\widetilde{K} &= 2p(p-1) \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \frac{w^{-1}(x_1) + w^{-1}(x_2)}{|x_1 - x_2|} \, dX \\
&= 4 \sum_{1 \leq i < j \leq p} \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \frac{w^{-1}(x_i) + w^{-1}(x_j)}{|x_i - x_j|} \, dX.
\end{aligned} \tag{77}$$

We can write

$$\begin{aligned}
&w^{-1}(x_i) + w^{-1}(x_j) = (w(x_i)w(x_j))^{-1}(w(x_i) + w(x_j)) \\
&= \sum_{s=1}^{K} \mu_s (w(x_i)|x_i - R_s|)^{-1} \big(w(x_j)|x_j - R_s|\big)^{-1} (|x_i - R_s| + |x_j - R_s|).
\end{aligned} \tag{78}$$

We use this and $|x_i - x_j| \leq |x_i - R_s| + |x_j - R_s|$ to say

$$\widetilde{U} - 2\widetilde{K} \geq 4 \sum_{i<j} \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \sum_{s=1}^{K} \mu_s g_s(x_i) g_s(x_j) \, dX, \tag{79}$$

where

$$g_s(x) = (w(x)|x - R_s|)^{-1}. \tag{80}$$

In particular, this means that

$$\begin{aligned}\gamma_s &= \int_{\mathbb{R}^3} \rho(x) g_s(x) dx = N \int_{\mathbb{R}^{3N}} |\psi(X)|^2 g_s(x_1)\, dX \\ &= 2p \int_{\mathbb{R}^{3N}} |\psi(X)|^2 g_s(x_1)\, dX \\ &= 2 \sum_{i=1}^{p} \int_{\mathbb{R}^{3N}} |\psi(X)|^2 g_s(x_i)\, dX, \end{aligned} \tag{81}$$

where, in the last line, we use symmetry of $|\psi(X)|^2$.

Using Lemma 3, with $f = g_s$ we have

$$\text{Re} \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \sum_{1 \le i < j \le p} g_s(x_i) g_s(x_j) dX \tag{82}$$

$$\geq \frac{1}{2} \left| \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \sum_{i=1}^{p} g_s(x_i) \right|^2 - \frac{1}{2} \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \sum_{i=1}^{p} g_s(x_i)^2\, dX. \tag{83}$$

Using this inequality we have

$$\begin{aligned}\widetilde{U} - 2\widetilde{K} \geq & 2 \sum_{s=1}^{K} \mu_s \left| \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \sum_{i=1}^{p} g_s(x_i)\, dX \right|^2 \\ & - 2 \sum_{s=1}^{K} \mu_s \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \sum_{i=1}^{p} g_s(x_i)^2 dX \\ = & \frac{1}{2} \sum_{s=1}^{K} \mu_s \left| 2 \sum_{i=1}^{p} \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 g_s(x_i)\, dX \right|^2 \\ & - \sum_{s=1}^{K} 2 \sum_{i=1}^{p} \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \mu_s g_s(x_i)^2\, dX. \end{aligned} \tag{84}$$

By our definition of w, we have

$$1 \geq \frac{\mu_s}{|x - R_s| w(x)} = \mu_s g_s(x). \tag{85}$$

Using this and recalling the definition of γ_s from (81) we obtain

$$\begin{aligned}\widetilde{U} - 2\widetilde{K} \geq & \frac{1}{2} \sum_{s=1}^{K} \mu_s \left| 2 \sum_{i=1}^{p} \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 g_s(x_i)\, dX \right|^2 \\ & - \sum_{s=1}^{K} 2 \sum_{i=1}^{p} \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 g_s(x_i)\, dX \\ = & \frac{1}{2} \sum_{s=1}^{K} \mu_s |\gamma_s|^2 - \sum_{s=1}^{K} \gamma_s. \end{aligned} \tag{86}$$

We also have an inequality for $\widetilde{U}$. Using the same methods as above, we have

$$\begin{aligned}\widetilde{U} &= 4\sum_{i=1}^{p}\sum_{j=1}^{p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} w(x)^{-1}\frac{|u_i(x)|^2|u_j(y)|^2}{|x-y|}dxdy \\ &= 2\sum_{i=1}^{p}\sum_{j=1}^{p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\left(w(x)^{-1}+w(y)^{-1}\right)\frac{|u_i(x)|^2|u_j(y)|^2}{|x-y|}dxdy \\ &= \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\left(w(x)^{-1}+w(y)^{-1}\right)\frac{\rho(x)\rho(y)}{|x-y|}dxdy \\ &\geq \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\left(\sum_{s=1}^{K}\mu_s g_s(x)g_s(y)\right)\rho(x)\rho(y)dxdy \\ &= \frac{1}{2}\sum_{s=1}^{K}\mu_s\gamma_s^2. \end{aligned} \tag{87}$$

Hence by (86) and (87), we have

$$\begin{aligned}\widetilde{U}-\widetilde{K} &= \frac{1}{2}\widetilde{U}+\frac{1}{2}\left(\widetilde{U}-2\widetilde{K}\right) \\ &\geq \frac{1}{2}\left(\frac{1}{2}\sum_{s=1}^{K}\mu_s\gamma_s^2\right)+\frac{1}{2}\left(\frac{1}{2}\sum_{s=1}^{K}\mu_s|\gamma_s|^2-\sum_{s=1}^{K}\gamma_s\right) \\ &= \frac{1}{2}\sum_{s=1}^{K}\left(\mu_s\gamma_s^2-\gamma_s\right). \end{aligned} \tag{88}$$

Thus, we obtain

$$\widetilde{V}+\widetilde{U}-\widetilde{K} \geq \frac{1}{2}\sum_{s=1}^{K}\gamma_s(\mu_s\gamma_s-1-2Z_s). \tag{89}$$

If we have a stable solution, it follows that

$$0 \geq \widetilde{V}+\widetilde{U}-\widetilde{K}. \tag{90}$$

Therefore, if we have a stable solution, it follows that

$$0 \geq \sum_{s=1}^{K}\gamma_s(\mu_s\gamma_s-1-2Z_s). \tag{91}$$

Let us define

$$\delta_s \equiv \mu_s\gamma_s/N, \tag{92}$$

$$\beta_s \equiv (2Z_s+1)/(2Z+1K). \tag{93}$$

We notice that

$$\begin{aligned}\sum_{s=1}^{K}\delta_s &= \frac{1}{N}\sum_{s=1}^{K}\mu_s\gamma_s \\ &= \frac{1}{N}\sum_{s=1}^{K}\mu_s\int_{\mathbb{R}^3}\rho(x)|x-R_s|^{-1}w(x)^{-1}dx \\ &= \frac{1}{N}\int_{\mathbb{R}^3}\rho(x)w(x)w(x)^{-1}dx = 1. \end{aligned} \tag{94}$$

We also have

$$\sum_{s=1}^{K} \beta_s = \frac{1}{Z2+K} \sum_{s=1}^{K} (2Z_s + 1)$$
$$= \frac{1}{2Z+K}(2Z+K) = 1. \tag{95}$$

Hence,

$$\sum_{s=1}^{K} \delta_s = \sum_{s}^{K} \beta_s. \tag{96}$$

We have that δ_s can be written directly in terms of μ_s, as γ_s depends on μ_s. So, suppose that we can choose $\{\mu_s\}_{1 \leq \sigma \leq K}$ so that for $s = 1 \ldots K$, we have

$$\delta_s = \beta_s. \tag{97}$$

We can do this as β_s is a constant based on the system. Then, we have

$$\sum_{s=1}^{K} \gamma_s(\mu_s \gamma - 2 - 2Z_s) = \sum_{s=1}^{K} \gamma_s \delta_s \left(N - \frac{1}{\beta_s}(2Z_s + 1) \right)$$
$$= \sum_{s=1}^{K} \gamma_s \delta_s (N - (2Z + K)). \tag{98}$$

Therefore, since $\gamma_s \geq 0$ and $\delta_s \geq 0$, a stable solution implies that

$$0 > N - (2Z + K), \tag{99}$$

whence $N < 2Z + K$. This completes the proof for the molecular RHF model.

8. Proof of Theorem 1 for the UHF Model

For UHF model, the point is in how we split up the $\widetilde{U} - \widetilde{K}$ term. For the UHF model we have

$$\begin{aligned}
\widetilde{U} =& \frac{1}{2} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\alpha} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{w(x) + w(y)}{|x-y|} |\phi_i^\alpha(x)|^2 |\phi_j^\alpha(y)|^2 dy dx \\
&+ \frac{1}{2} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{w(x) + w(y)}{|x-y|} |\phi_i^\alpha(x)|^2 |\phi_j^\beta(y)|^2 dy dx \\
&+ \frac{1}{2} \sum_{i=1}^{N_\beta} \sum_{j=1}^{N_\alpha} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{w(x) + w(y)}{|x-y|} |\phi_i^\beta(x)|^2 |\phi_j^\alpha(y)|^2 dy dx \\
&+ \frac{1}{2} \sum_{i=1}^{N_\beta} \sum_{j=1}^{N_\beta} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{w(x) + w(y)}{|x-y|} |\phi_i^\beta(x)|^2 |\phi_j^\beta(y)|^2 dy dx.
\end{aligned} \tag{100}$$

We note that by relabelling we have

$$\begin{aligned}
&\sum_{i=1}^{N_\beta}\sum_{j=1}^{N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}|\phi_i^\beta(x)|^2|\phi_j^\alpha(y)|^2dydx\\
=&\sum_{j=1}^{N_\beta}\sum_{i=1}^{N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}|\phi_j^\beta(x)|^2|\phi_i^\alpha(y)|^2dydx\\
=&\sum_{j=1}^{N_\beta}\sum_{i=1}^{N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(y)+w(x)}{|y-x|}|\phi_j^\beta(y)|^2|\phi_i^\alpha(x)|^2dxdy\\
=&\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}|\phi_i^\alpha(x)|^2|\phi_j^\beta(y)|^2dydx. \qquad (101)
\end{aligned}$$

Hence,

$$\begin{aligned}
\widetilde{U}=&\frac{1}{2}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}|\phi_i^\alpha(x)|^2|\phi_j^\alpha(y)|^2dydx\\
&+\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}|\phi_i^\alpha(x)|^2|\phi_j^\beta(y)|^2dydx\\
&+\frac{1}{2}\sum_{i=1}^{N_\beta}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}|\phi_i^\beta(x)|^2|\phi_j^\beta(y)|^2dydx. \qquad (102)
\end{aligned}$$

For $\widetilde{K}$, we have

$$\begin{aligned}
\widetilde{K}=&\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)}{|x-y|}\phi_i^\alpha(x)\phi_i^\alpha(y)\phi_j^\alpha(x)\phi_j^\alpha(y)dydx\\
&+\sum_{i=1}^{N_\beta}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)}{|x-y|}\phi_i^\beta(x)\phi_i^\beta(y)\phi_j^\beta(x)\phi_j^\beta(y)dydx\\
=&\frac{1}{2}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}\phi_i^\alpha(x)\phi_i^\alpha(y)\phi_j^\alpha(x)\phi_j^\alpha(y)dydx\\
&+\frac{1}{2}\sum_{i=1}^{N_\beta}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}\phi_i^\beta(x)\phi_i^\beta(y)\phi_j^\beta(x)\phi_j^\beta(y)dydx. \qquad (103)
\end{aligned}$$

Thus, using Corollary 2 with $F(x,y) = \frac{w(x)+w(y)}{|x-y|}$, and the fact that $\frac{1}{2}\sum_{i\neq j} = \sum_{i<j}$ we have that

$$\begin{aligned}
&\widetilde{U} - \widetilde{K} \\
=&\frac{1}{2}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}\left(|\phi_i^\alpha(x)|^2|\phi_j^\alpha(y)|^2 - \phi_i^\alpha(x)\phi_j^\alpha(x)\phi_j^\alpha(y)\phi_i^\alpha(y)\right)dxdy \\
&+\frac{1}{2}\sum_{i=1}^{N_\beta}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}\left(|\phi_i^\beta(x)|^2|\phi_j^\beta(y)|^2 - \phi_i^\beta(x)\phi_j^\beta(x)\phi_j^\beta(y)\phi_i^\beta(y)\right)dxdy \\
&+\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}|\phi_i^\alpha(x)|^2|\phi_j^\beta(y)|^2dydx \\
=&\sum_{1\leq i<j\leq N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}\left(|\phi_i^\alpha(x)|^2|\phi_j^\alpha(y)|^2 - \phi_i^\alpha(x)\phi_j^\alpha(x)\phi_j^\alpha(y)\phi_i^\alpha(y)\right)dxdy \\
&+\sum_{1\leq i<j\leq N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}\left(|\phi_i^\beta(x)|^2|\phi_j^\beta(y)|^2 - \phi_i^\beta(x)\phi_j^\beta(x)\phi_j^\beta(y)\phi_i^\beta(y)\right)dxdy \\
&+\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}|\phi_i^\alpha(x)|^2|\phi_j^\beta(y)|^2dydx \\
=&\left(\frac{1}{2}N(N-1) - N_\alpha N_\beta\right)\sum_\sigma\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2\frac{w(x_1)+w(x_2)}{|x_1-x_2|}dX \\
&+\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{w(x)+w(y)}{|x-y|}|\phi_i^\alpha(x)|^2|\phi_j^\beta(y)|^2dydx. \qquad (104)
\end{aligned}$$

The next idea is that we will choose a good function w in order to get a triangle inequality. We shall first do the atomic case, followed by the molecular case.

8.1. Atomic UHF Model

For the atomic case, we have $w(x) = |x|$, and therefore

$$\frac{w(x_1)+w(x_2)}{|x_1-x_2|} = \frac{w|x_1|+w|x_2|}{|x_1-x_2|} \geq 1. \qquad (105)$$

Using the orthonormality of the single particle wave functions ϕ_i^α and ϕ_j^β, we obtain

$$\begin{aligned}
&\widetilde{U} - \widetilde{K} \\
\geq&\left(\frac{1}{2}N(N-1) - N_\alpha N_\beta\right)\sum_{\sigma\in S^N}\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2\,dX \\
&+\sum_{i=1}^{N_\alpha}\int_{\mathbb{R}^3}|\phi_i^\alpha(x)|^2dx\sum_{j=1}^{N_\beta}\int_{\mathbb{R}^3}|\phi_j^\beta(y)|^2dy \\
=&\left(\frac{1}{2}N(N-1) - N_\alpha N_\beta\right) + N_\alpha N_\beta \qquad (106) \\
=&\frac{1}{2}N(N-1). \qquad (107)
\end{aligned}$$

Since we have $\widetilde{V} = -ZN$ in the atomic case, we have

$$0 > \widetilde{V} + \widetilde{U} - \widetilde{K} \geq -ZN + \frac{1}{2}N(N-1), \qquad (108)$$

and therefore

$$N < 2Z + 1. \tag{109}$$

8.2. Molecular UHF Model

For the corresponding result in the molecular case, we define γ_s, μ_s, and g_s as in Section 7. However, if we apply Corollary 2, we have that

$$\begin{aligned}
&\widetilde{U} - \widetilde{K} \\
&= \left(\frac{1}{2}N(N-1) - N_\alpha N_\beta\right) \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \frac{w(x_1) + w(x_2)}{|x_1 - x_2|}\, dX \\
&\quad + \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{w(x) + w(y)}{|x-y|} |\phi_i^\alpha(x)|^2 |\phi_j^\beta(y)|^2 dy dx \\
&= \frac{1}{2}N(N-1) \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \frac{w(x_1) + w(x_2)}{|x_1 - x_2|}\, dX.
\end{aligned} \tag{110}$$

Therefore, we can apply the triangle inequality as in Section 7 to obtain

$$\widetilde{U} - \widetilde{K} \geq \frac{1}{2}N(N-1) \sum_{\sigma \in S^N} \int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 \sum_{s=1}^{K} \mu_s g_s(x_1) g_s(x_2)\, dX, \tag{111}$$

and we thus follow the same argument as before.

9. Proof of Theorem 2

We will now give the proof of Theorem 2.

Proof. We note that if it is true that

$$0 > \widetilde{V} + 2\left(\widetilde{U} - 2\widetilde{K}\right), \tag{112}$$

then the triangle inequality from (66) will imply that

$$0 > -2pZ + 2 \times 2p(p-1), \tag{113}$$

which in turn implies

$$Z + 2 > N. \tag{114}$$

However, we note that if assumption (12) holds, then by multiplying both sides by 2 we arrive at

$$\widetilde{T} + 3\widetilde{K} - \widetilde{U} \geq 0, \tag{115}$$

and so

$$\begin{aligned}
0 \geq \widetilde{T} + \widetilde{V} + \widetilde{U} - \widetilde{K} &= \left(\widetilde{T} + 3\widetilde{K} - \widetilde{U}\right) + \widetilde{V} + 2\left(\widetilde{U} - 2\widetilde{K}\right) \\
&\geq \widetilde{V} + 2\left(\widetilde{U} - 2\widetilde{K}\right).
\end{aligned} \tag{116}$$

But this means (112) is true, and so the result follows. □

Remark 1. *We remark that condition* (12) *holds in the case where* $p = 1$.
Indeed, plugging $p = 1$ *into Equations* (58) *and* (59)*, we have that*

$$\widetilde{U} = 4 \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} |x| \frac{|u_1(x)|^2 |u_1(x')|^2}{|x - x'|} dx dx' \tag{117}$$

and

$$\widetilde{K} = 2\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} |x| \frac{\overline{u_1(x)}u_1(x')u_1(x)\overline{u_1(x')}}{|x-x'|} dxdx'. \tag{118}$$

Therefore,

$$3\widetilde{K} - \widetilde{U} = 2\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} |x| \frac{|u_1(x)|^2|u_1(x')|^2}{|x-x'|} dxdx' \geq 0, \tag{119}$$

and since $\tilde{T} \geq 0$*, it follows that*

$$\widetilde{T} + 3\widetilde{K} - \widetilde{U} \geq 0. \tag{120}$$

Thus we have shown that if $p = 1$ *(i.e., for two electrons) then Equation* (115) *is true, and therefore condition* (12) *is fulfilled. From a physical point of view, it is worth noting that for a two-electron closed shell atom (such as helium) there is no exchange term as K arises from the Pauli principle and there are no same spin electrons in such systems.*

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Appendix A

In this appendix we give proofs of the auxiliary results in Section 3.

Proof of Lemma 2. For the RHF model, we wish to show that there exists a constant $\widetilde{N}$ depending on N only, so that

$$\begin{aligned}&\widetilde{N}\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)\,dX \\ &= \sum_{1\leq i<j\leq N}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\left(|\phi_i(x)|^2|\phi_j(y)|^2 - \overline{\phi_i(x)}\phi_j(x)\phi_i(y)\overline{\phi_j(y)}\right)F(x,y)\,dxdy.\end{aligned} \tag{A1}$$

However, we start by proving the UHF case, as the RHF model is a special case where the single-particle wave functions coincide with each other. Hence, for $i = 1,\ldots,N$ the single-particle wave functions are given by

$$u_i(x,\sigma) = \begin{cases}\phi_i^\alpha(x)\alpha(\sigma) & i \leq N_\alpha \\ \phi_{i-N_\alpha}^\beta(x)\beta(\sigma) & i > N_\alpha\end{cases}, \tag{A2}$$

where N_α was defined in (41). For the N-particle case, we have that

$$\psi = \frac{1}{\sqrt{N!}}\det(u_i(x_j,\sigma_j)). \tag{A3}$$

We write $\mathcal{E}_N$ for the space of permutations of length N and $\mathrm{sgn}(e)$ for the sign of the permutation $e \in \mathcal{E}_N$. We take a fixed σ which we choose so that the single-particle wave functions are nonzero. In other words, for the RHF model we have

$$\sigma_j = \begin{cases}+ & j \leq p \\ - & j > p\end{cases} \tag{A4}$$

and for UHF we have

$$\sigma_j = \begin{cases} + & j \leq N_\alpha \\ - & j > N_\alpha. \end{cases} \tag{A5}$$

We now expand the left-hand side of (A1).

$$\begin{aligned} &\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)\,dX = \frac{1}{N!}\int_{\mathbb{R}^{3N}} |\det(u(X,\sigma))|^2 F(x_1,x_2)\,dX \\ =&\frac{1}{N!}\int_{\mathbb{R}^{3N}} \left|\sum_{e\in\mathcal{E}_N} \operatorname{sgn}(e)\prod_{i=1}^{N} u_i(x_{e_i},\sigma_{e_i})\right|^2 F(x_1,x_2)\,dX \\ =&\frac{1}{N!}\int_{\mathbb{R}^{3N}} \overline{\left(\sum_{e\in\mathcal{E}_N} \operatorname{sgn}(e)\prod_{i=1}^{N} u_i(x_{e_i},\sigma_{e_i})\right)} \\ &\times\left(\sum_{e'\in\mathcal{E}_N} \operatorname{sgn}(e')\prod_{i=1}^{N} u_i(x_{e'_i},\sigma_{e'_i})\right) F(x_1,x_2)\,dX. \end{aligned} \tag{A6}$$

We take the sums outside of the products and arrive at

$$\frac{1}{N!}\sum_{e\in\mathcal{E}_N}\sum_{e'\in\mathcal{E}_N} \operatorname{sgn}(e)\operatorname{sgn}(e')\int_{\mathbb{R}^{3N}} \prod_{i=1}^{N}\prod_{j=1}^{N} \overline{u_i(x_{e_i},\sigma_{e_i})}u_j(x_{e'_j},\sigma_{e'_j})F(x_1,x_2)\,dX. \tag{A7}$$

Because e is a permutation in $\mathcal{E}_N$, there exists a unique $f \in \mathcal{E}_N$ so that for $i = 1,\ldots,N$ we have

$$e_{f_i} = i. \tag{A8}$$

Because this f is uniquely determined, there exists a bijection between $e \in \mathcal{E}_N$ and $f \in \mathcal{E}_N$, and hence

$$\sum_{e\in\mathcal{E}_N}\prod_{i=1}^{N} u_i(x_{e_i},\sigma_{e_i}) = \sum_{f\in\mathcal{E}_N}\prod_{i=1}^{N} u_{f_i}(x_i,\sigma_i). \tag{A9}$$

We have an equivalent result for e' to f'. When we also combine the products, we have that

$$\begin{aligned} &\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)\,dX \\ =&\frac{1}{N!}\sum_{f\in\mathcal{E}_N}\sum_{f'\in\mathcal{E}_N} \operatorname{sgn}(f)\operatorname{sgn}(f')\int_{\mathbb{R}^{3N}} F(x_1,x_2)\prod_{i=1}^{N}\overline{u_{f_i}(x_i,\sigma_i)}u_{f'_i}(x_i,\sigma_i)\,dX. \end{aligned} \tag{A10}$$

Next we consider the spin terms. For the UHF model, recall that spin is positive for $i \leq N_\alpha$ and negative for $i > N_\alpha$. So, in particular, for

$$u_i(x_{e_i},\sigma_{e_i}) \tag{A11}$$

to be nonzero, we require that

$$\begin{cases} e_i \in \{1,\ldots,N_\alpha\} & i \leq N_\alpha \\ e_i \in \{N_\alpha+1,\ldots,N\} & i > N_\alpha \end{cases}. \tag{A12}$$

Since any zero term will make the whole product zero, we conclude that for the UHF model,

$$\sum_{f\in\mathcal{E}_N} = \sum_{f\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}}, \tag{A13}$$

where $\mathcal{E}_{N_\alpha} \times \mathcal{E}_{N_\beta} \subset \mathcal{E}_N$ is the set of permutations that have distinct "cycles" of length N_α and N_β. Hence we remove spin dependence and get that

$$\begin{aligned}&\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)\,dX \\ &\quad= \frac{1}{N!}\sum_{f\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}}\sum_{f'\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}} \operatorname{sgn}(f)\operatorname{sgn}(f')\int_{\mathbb{R}^{3N}} F(x_1,x_2)\prod_{i=1}^{N}\overline{u_{f_i}(x_i)}u_{f'_i}(x_i)\,dX.\end{aligned}$$

For $i \geq 3$, we can factorise the integral over dx_i out of the above, namely we have

$$\int_{\mathbb{R}^3} \overline{u_{f_i}(x_i,\sigma_i)}u_{f'_i}(x_i,\sigma_i)dx_i. \tag{A14}$$

If u_{f_i} and $u_{f'_i}$ are of the same sign, then as discussed in Section 5 the Kronecker delta condition implies that

$$\delta_{f_i,f_j} = \int_{\mathbb{R}^3} \overline{u_{f_i}(x_i,\sigma_i)}u_{f'_i}(x_i,\sigma_i)\,dx_i. \tag{A15}$$

However if u_{f_i} and $u_{f'_i}$ are of different sign types, then because the σ_i is evaluated by both wave functions, it automatically follows that the integral in (A14) is trivial. Thus Equation (A15) holds for all $i, j \leq N$.

Since this is HF theory, the space components of the single-particle wave functions are still orthogonal. Since even a single zero term will cause the product to be zero, we conclude that for $i \geq 3$, we must have $f'_i = f_i$, and hence

$$\begin{aligned}&\sum_{f\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}}\sum_{f'\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}} \operatorname{sgn}(f)\operatorname{sgn}(f')\int_{\mathbb{R}^{3N}} F(x_1,x_2)\prod_{i=1}^{N}\overline{u_{f_i}(x_i)}u_{f'_i}(x_i)dX \\ &\qquad= \sum_{f\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}}\sum_{f'\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}} \operatorname{sgn}(f)\operatorname{sgn}(f') \\ &\qquad\quad\times\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x_1,x_2)\overline{u_{f_1}(x_1)}u_{f'_1}(x_1)\overline{u_{f_2}(x_2)}u_{f'_2}(x_2)dx_1dx_2 \\ &\qquad\quad\times\prod_{i=3}^{N}\int_{\mathbb{R}^3}\overline{u_{f_i}(x_i)}u_{f'_i}(x_i)dx_i \\ &\qquad= \sum_{f\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}}\sum_{\substack{f'\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}\\ f'_i=f_i,i\geq 3}} \operatorname{sgn}(f)\operatorname{sgn}(f') \\ &\qquad\quad\times\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x_1,x_2)\overline{u_{f_1}(x_1)}u_{f'_1}(x_1)\overline{u_{f_2}(x_2)}u_{f'_2}(x_2)dx_1dx_2.\end{aligned} \tag{A16}$$

At this point the sharp-eyed reader might protest that, since we assume that $i \geq 3$, and we sum i up to N, we are implicitly assuming that $N \geq 3$. Thus, we here note that the above result still holds for the case $N = 2$ because in this case $f'_i = f_i$ trivially holds for $i = 1, 2$.

We have that f' is a permutation determined by f up to two terms, because all the other terms are accounted for. Hence we know that the first two terms of ϕ' must be taken from $\{f_1, f_2\}$. If we have $f'_1 = f_1$ and $f'_2 = f_2$, then the permutation signs of f and f' are the same, and hence the product will be 1. Conversely if $f'_1 = f_2$ and $f'_2 = f_1$, the permutation signs are different and their product will be -1. Hence the above becomes

$$
\begin{aligned}
&\frac{1}{N!}\sum_{f\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}}\sum_{\substack{f'\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}\\ f'_i=f_i,i\geq 3}}\operatorname{sgn}(f)\operatorname{sgn}(f')\\
&\quad\times\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(x_1,x_2)\overline{u_{f_1}(x_1)}u_{f'_1}(x_1)\overline{u_{f_2}(x_2)}u_{f'_2}(x_2)dx_1dx_2.\\
&=\frac{1}{N!}\sum_{f\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}}\left(\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(x_1,x_2)\overline{u_{f_1}(x_1)}u_{f_1}(x_1)\overline{u_{f_2}(x_2)}u_{f_2}(x_2)dx_1dx_2\right.\\
&\quad\left.-\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(x_1,x_2)\overline{u_{f_1}(x_1)}u_{f_2}(x_1)u_{f_1}(x_2)\overline{u_{f_2}(x_2)}dx_1dx_2\right)\\
&=\frac{1}{N!}\sum_{f_1\neq f_2}^{N_\alpha}\times(N_\alpha-2)!(N_\beta)!\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(x_1,x_2)\left(|u_{f_1}(x_1)|^2|u_{f_2}(x_2)|^2\right.\\
&\quad\left.-\overline{u_{f_1}(x_1)}u_{f_2}(x_1)u_{f_1}(x_2)\overline{u_{f_2}(x_2)}\right)dx_1dx_2\\
&=\frac{2(N_\alpha-2)!(N_\beta)!}{(N)!}\sum_{1\leq i<j\leq N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(x,y)\left(|\phi_i^\alpha(x)|^2|\phi_j^\alpha(y)|^2\right.\\
&\quad\left.-\overline{\phi_i^\alpha(x)}\phi_j^\alpha(x)\phi_i^\alpha(y)\overline{\phi_j^\alpha(y)}\right)dxdy,
\end{aligned}
$$

where in the final line we relabelled the suffixes f_1 and f_2 to i and j. By the symmetry of the notations of N_α and N_β, we have the corresponding result

$$
\begin{aligned}
&\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2F(x_1,x_2)\,dX\\
&\quad=\frac{2(N_\beta-2)!(N_\alpha)!}{(N)!}\sum_{1\leq i<j\leq N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(x,y)\left(|\phi_i^\beta(x)|^2|\phi_j^\beta(y)|^2\right.\\
&\qquad\left.-\overline{\phi_i^\beta(x)}\phi_j^\beta(x)\phi_i^\beta(y)\overline{\phi_j^\beta(y)}\right)dxdy.
\end{aligned}
\tag{A17}
$$

Thus for the UHF model we have

$$
\begin{aligned}
&\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2F(x_1,x_2)\,dX\\
=&\widetilde{N}_1\sum_{1\leq i<j\leq N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(x,y)\left(|\phi_i^\alpha(x)|^2|\phi_j^\alpha(y)|^2-\overline{\phi_i^\alpha(x)}\phi_j^\alpha(x)\phi_i^\alpha(y)\overline{\phi_j^\alpha(y)}\right)dxdy\\
&+\widetilde{N}_2\sum_{1\leq i<j\leq N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(x,y)\left(|\phi_i^\beta(x)|^2|\phi_j^\beta(y)|^2-\overline{\phi_i^\beta(x)}\phi_j^\beta(x)\phi_i^\beta(y)\overline{\phi_j^\beta(y)}\right)dxdy,
\end{aligned}
\tag{A18}
$$

where

$$
\widetilde{N}_1=\frac{(N_\alpha-2)!(N_\beta)!}{N!} \tag{A19}
$$

$$
\widetilde{N}_2=\frac{(N_\beta-2)!(N_\alpha)!}{N!}. \tag{A20}
$$

By setting $N_\alpha=N_\beta=p$ and $\phi_i^\alpha=\phi_i^\beta=\phi_i$, we arrive at the corresponding result for the RHF model, namely

$$
\begin{aligned}
&\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2F(x_1,x_2)dX\\
=&\frac{1}{\widetilde{N}}\sum_{1\leq i<j\leq p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}F(x,y)\left(|\phi_i(x)|^2|\phi_j(y)|^2-\overline{\phi_i(x)}\phi_j(x)\phi_i(y)\overline{\phi_j(y)}\right)dxdy,
\end{aligned}
\tag{A21}
$$

where

$$\widetilde{N} = \frac{(2p)!}{2(p-2)!p!}. \tag{A22}$$

This completes the proof. □

Remark A1. *We note that in the case of p pairs (with opposite spins) of electrons, that is, the RHF model with $N_\beta = p = N_\alpha$, we arrive at*

$$\frac{1}{2}N(N-1)\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)dX = \widetilde{U} - \widetilde{K}. \tag{A23}$$

which is the result Lieb arrives at in [13]; here $\widetilde{U}$ and $\widetilde{K}$ are defined in (53).

Proof of Corollary 2, Assertion 1. We now consider the version where we sum over $\sigma \in S^N$ and we are in the RHF model.

$$\sum_{\sigma\in S^N}\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)dX. \tag{A24}$$

We proceed with the same analysis as in the proof of Lemma 2 up to Equation (A10), and we arrive at

$$\begin{aligned} &N!\sum_{\sigma\in S^N}\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)dX \\ &= \sum_{\sigma\in S^N}\sum_{f\in\mathcal{E}_N}\sum_{f'\in\mathcal{E}_N} \operatorname{sgn}(f)\operatorname{sgn}(f')\int_{\mathbb{R}^{3N}} F(x_1,x_2)\prod_{i=1}^{N}\overline{u_{f_i}(x_i,\sigma_i)}u_{f_i'}(x_i,\sigma_i)dX. \end{aligned} \tag{A25}$$

Let us consider which σ will give a non-trivial result. Since we are considering the RHF model, $\sigma \in S^N$ will need to have p terms of positive spin and p terms of negative spin.

Let us now make another permutation transform on the f and f', to say g and g', in order that, given σ, we have that the first p terms have positive spin, and the final p terms have negative spin. But this is now exactly the case we have already solved for.

So, the only non-trivial spin combinations are those that have exactly N_α positive spin terms. In other words, we choose N_α electrons out of N to have positive. Hence

$$\sum_{f\in\mathcal{E}_N}\sum_{f'\in\mathcal{E}_N} = \frac{N!}{p!(N-p)!} = \frac{(2p)!}{(p!)(p!)}. \tag{A26}$$

Hence, by invoking Lemma 2, we obtain

$$\begin{aligned} &\sum_{\sigma\in S^N}\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)\,dX \\ &= \frac{(2p)!}{(p!)(p!)}\frac{1}{\widetilde{N}}\sum_{1\le i<j\le p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x,y)\left(|\phi_i(x)|^2|\phi_j(y)|^2 - \overline{\phi_i(x)}\phi_j(x)\phi_i(y)\overline{\phi_j(y)}\right)dxdy, \\ &= \frac{(2p)!}{(p!)(p!)}\frac{2(p-2)!p!}{(2p)!}\sum_{1\le i<j\le p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x,y)\Big(|\phi_i(x)|^2|\phi_j(y)|^2 \\ &\quad - \overline{\phi_i(x)}\phi_j(x)\phi_i(y)\overline{\phi_j(y)}\Big)dxdy, \\ &= \frac{2}{p(p-1)}\sum_{1\le i<j\le p}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x,y)\left(|\phi_i(x)|^2|\phi_j(y)|^2 - \overline{\phi_i(x)}\phi_j(x)\phi_i(y)\overline{\phi_j(y)}\right)dxdy. \end{aligned} \tag{A27}$$

□

Proof of Corollary 2, Assertion 2. Given a spin $\sigma \in \mathcal{E}_{N_\alpha} \times \mathcal{E}_{N_\beta} \subset S^N$, we have

$$\begin{aligned}&\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)dX\\ =&\frac{2(N_\alpha-2)!(N_\beta)!}{(N)!}\sum_{1\le i<j\le N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x,y)\Big(|\phi_i^\alpha(x)|^2|\phi_j^\alpha(y)|^2\\ &-\overline{\phi_i^\alpha(x)}\phi_j^\alpha(x)\phi_i^\alpha(y)\overline{\phi_j^\alpha(y)}\Big)dxdy.\end{aligned} \tag{A28}$$

If $\sigma \notin \mathcal{E}_{N_\alpha} \times \mathcal{E}_{N_\beta}$, then by the (pigeonhole) argument in Corollary 2 it follows that

$$\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)dX = 0. \tag{A29}$$

Hence for the UHF model, using the fact that we have N electrons and we choose N_α to have positive spin, we have

$$\begin{aligned}&\sum_{\sigma\in\mathcal{E}_N}\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)dX = \sum_{\sigma\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}}\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)dX\\ &=\frac{(N)!}{(N_\alpha)!(N-N_\alpha)!}\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)dX\\ &=\frac{2(N_\alpha-2)!}{(N_\alpha)!}\\ &\sum_{1\le i<j\le N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x,y)\Big(|\phi_i^\alpha(x)|^2|\phi_j^\alpha(y)|^2-\overline{\phi_i^\alpha(x)}\phi_j^\alpha(x)\phi_i^\alpha(y)\overline{\phi_j^\alpha(y)}\Big)dxdy.\end{aligned} \tag{A30}$$

Since we could just as well choose N_β electrons to have negative spin, choosing the integral with the β terms gives us

$$\begin{aligned}&\sum_{\sigma\in\mathcal{E}_N}\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_1,x_2)dX\\ &=\frac{2(N_\beta-2)!}{(N_\beta)!}\\ &\sum_{1\le i<j\le N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x,y)\Big(|\phi_i^\beta(x)|^2|\phi_j^\beta(y)|^2-\overline{\phi_i^\beta(x)}\phi_j^\beta(x)\phi_i^\beta(y)\overline{\phi_j^\beta(y)}\Big)dxdy.\end{aligned} \tag{A31}$$

Hence, it follows that

$$\begin{aligned}&\sum_{1\le i<j\le N_\alpha}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x,y)\Big(|\phi_i^\alpha(x)|^2|\phi_j^\alpha(y)|^2-\overline{\phi_i^\alpha(x)}\phi_j^\alpha(x)\phi_i^\alpha(y)\overline{\phi_j^\alpha(y)}\Big)dxdy\\ &+\sum_{1\le i<j\le N_\beta}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} F(x,y)\Big(|\phi_i^\beta(x)|^2|\phi_j^\beta(y)|^2-\overline{\phi_i^\beta(x)}\phi_j^\beta(x)\phi_i^\beta(y)\overline{\phi_j^\beta(y)}\Big)dxdy\\ &=\frac{1}{2}\left(\frac{(N_\alpha)!}{(N_\alpha-2)!}+\frac{(N_\beta)!}{(N_\beta-2)!}\right)\sum_{\sigma\in\mathcal{E}_N}\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2F(x_1,x_2)\,dX\\ &=\frac{1}{2}\big(N_\alpha(N_\alpha-1)+N_\beta(N_\beta-1)\big)\sum_{\sigma\in\mathcal{E}_N}\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2F(x_1,x_2)dX\\ &=\frac{1}{2}\Big((N_\alpha+N_\beta)^2-(N_\alpha+N_\beta)-2N_\alpha N_\beta\Big)\sum_{\sigma\in\mathcal{E}_N}\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2F(x_1,x_2)\,dX\\ &=\left(\frac{1}{2}N(N-1)-N_\alpha N_\beta\right)\sum_{\sigma\in\mathcal{E}_N}\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2F(x_1,x_2)\,dX.\end{aligned} \tag{A32}$$

This proves the corollary. □

Proof of Lemma 1. By the definition of ψ and the determinant function, we have that

$$\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_p,x_q)\,dX = \frac{1}{N!}\int_{\mathbb{R}^{3N}} |\det u(X,\sigma)|^2 F(x_p,x_q)\,dX$$
$$= \frac{1}{N!}\sum_{e\in\mathcal{E}_N}\sum_{e'\in\mathcal{E}_N}\operatorname{sgn}(e)\operatorname{sgn}(e')\int_{\mathbb{R}^{3N}} F(x_p,x_q)\prod_{i=1}^{N}\overline{u_i(x_{e_i},\sigma_{e_i})}u_i(x_{e'_i},\sigma_{e'_i})dX. \tag{A33}$$

By using the bijection of e to f defined by

$$e_{f_i} = i, \tag{A34}$$

we have

$$\frac{1}{N!}\sum_{e\in\mathcal{E}_N}\operatorname{sgn}(e)\operatorname{sgn}(e')\sum_{e'\in\mathcal{E}_N}\int_{\mathbb{R}^{3N}} F(x_p,x_q)\prod_{i=1}^{N}\overline{u_i(x_{e_i},\sigma_{e_i})}u_i(x_{e'_i},\sigma_{e'_i})\,dX$$
$$= \frac{1}{N!}\sum_{f\in\mathcal{E}_N}\sum_{f'\in\mathcal{E}_N}\operatorname{sgn}(f)\operatorname{sgn}(f')\int_{\mathbb{R}^{3N}} F(x_p,x_q)\prod_{i=1}^{N}\overline{u_{f_i}(x_i,\sigma_i)}u_{f'_i}(x_i,\sigma_i)\,dX$$
$$= \frac{1}{N!}\sum_{f\in\mathcal{E}_N}\sum_{f'\in\mathcal{E}_N}\operatorname{sgn}(f)\operatorname{sgn}(f')$$
$$\int_{\mathbb{R}^3} F(x_p,x_q)\overline{u_{f_i}(x_p,\sigma_p)}u_{f'_i}(x_p,\sigma_p)\overline{u_{f_i}(x_q,\sigma_q)}u_{f'_i}(x_q,\sigma_q)dx_p dx_q$$
$$\prod_{i=1,i\neq p,q}^{N}\int_{\mathbb{R}^3}\overline{u_{f_i}(x_i,\sigma_i)}u_{f'_i}(x_i,\sigma_i)dx_i. \tag{A35}$$

Because of our definition of σ, to have a non trivial term we require for all f, and correspondingly for f', that

$$\sigma_{f_i} = \begin{cases} +, & \text{when } i \le N_\alpha \\ -, & \text{when } i > N_\alpha \end{cases}. \tag{A36}$$

To this end, we see that such an f will belong in the subset

$$f \in \mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}\subset\mathcal{E}_N. \tag{A37}$$

We have the same result for f'.

Next, because the u_i are orthonormal, we see that in order for the term

$$\prod_{\substack{i=1\\ i\neq p,q}}^{N}\int_{\mathbb{R}^3}\overline{u_{f_i}(x_i,\sigma_i)}u_{f'_i}(x_i,\sigma_i)dx_i \tag{A38}$$

to be non-trivial, we require that $f'_i = f_i$ for $i \neq p,q$. Moreover, because of our choice in σ, the term will simply become

$$\prod_{\substack{i=1\\ i\neq p,q}}^{N}\int_{\mathbb{R}^3}\overline{u_{f_i}(x_i,\sigma_i)}u_{f'_i}(x_i,\sigma_i)dx_i = 1. \tag{A39}$$

Hence, we arrive at

$$\begin{aligned}
&\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_p,x_q)\,dX \\
&= \frac{1}{N!} \sum_{f\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}} \sum_{\substack{f'\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta} \\ f'_i=\phi_i \text{ for } i\neq p,q}} \operatorname{sgn}(f)\operatorname{sgn}(f') \\
&\int_{\mathbb{R}^3} F(x_p,x_q)\overline{u_{f_p}(x_p,\sigma_p)}u_{f'_p}(x_p,\sigma_p)\overline{u_{f_q}(x_q,\sigma_q)}u_{f'_q}(x_q,\sigma_q)dx_p dx_q. \qquad \text{(A40)}
\end{aligned}$$

So, the only free terms for f' are f'_p and f'_q. If we have $f'_p = f_p$ (and therefore we are forced to have $f'_q = f_q$), then $f' = f$, and so their permutation signs will be the same, $\operatorname{sgn}(f) = \operatorname{sgn}(f')$, and hence

$$\operatorname{sgn}(f)\operatorname{sgn}(f') = 1. \qquad \text{(A41)}$$

Otherwise, we have $f'_p = f_q$ (and therefore we are forced to have $f'_q = f_p$), and the signs of the terms will be opposite of each other, and hence

$$\operatorname{sgn}(f)\operatorname{sgn}(f') = -1. \qquad \text{(A42)}$$

Therefore,

$$\begin{aligned}
&\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_p,x_q)\,dX \\
&= \frac{1}{N!} \sum_{f\in\mathcal{E}_{N_\alpha}\times\mathcal{E}_{N_\beta}} \int_{\mathbb{R}^3} F(x_p,x_q)|u_{f_p}(x_p,\sigma_p)|^2|u_{f_q}(x_q,\sigma_q)|^2 dx_p dx_q \\
&- \int_{\mathbb{R}^3} F(x_p,x_q)\overline{u_{f_p}(x_p,\sigma_p)}u_{f_q}(x_p,\sigma_p)\overline{u_{f_q}(x_q,\sigma_q)}u_{f_p}(x_q,\sigma_q)dx_p dx_q. \qquad \text{(A43)}
\end{aligned}$$

If we now add the assumption that u_p and u_q have different signs, we see that we are free to choose $N_\alpha - 1$ positive spin terms and $N_\beta - 1$ negative spin terms. In addition, because u_p and u_q are of different signs, if we give both of them the same signed spin, the product will be zero, that is,

$$\overline{u_{f_q}(x_q,\sigma_q)}u_{f_p}(x_q,\sigma_q) = 0. \qquad \text{(A44)}$$

Since we are summing over the N_α positive spin terms u_p and the N_β negative spin terms u_q, we arrive at

$$\begin{aligned}
&\int_{\mathbb{R}^{3N}} |\psi(X,\sigma)|^2 F(x_p,x_q)dX \\
&= \frac{(N_\alpha-1)!(N_\beta-1)!}{N!} \sum_{p=1}^{N_\alpha}\sum_{q=1}^{N_\beta} \int_{\mathbb{R}^3} F(x_p,x_q)|\phi_p^\alpha(x_p)\alpha(\sigma_p)|^2|\phi_q^\beta(x_q)\beta(\sigma_q)|^2 dx_p dx_q. \qquad \text{(A45)}
\end{aligned}$$

□

Proof of Corollary 2. By the pigeonhole principle, any $\sigma \in S^N$ that gives a nontrivial result will have to have N_α positive spin terms and N_β negative spin terms. However, this means that given the f_i in the proof of Lemma 1, we can find a g_i so that

$$\sigma_{g_i} = \begin{cases} +, & \text{when } i \leq N_\alpha \\ -, & \text{when } i > N_\alpha \end{cases}. \qquad \text{(A46)}$$

when we consider the number of admissible spins, it is equivalent to the number of spins where we have N_α positive spins. Thus, there are N choose N_α, that is, $\binom{N}{N_\alpha}$ possible spin combinations. Hence,

$$\begin{aligned}
&\sum_{\sigma\in S^N}\int_{\mathbb{R}^{3N}}|\psi(X,\sigma)|^2F(x_p,x_q)\,dX\\
&=\binom{N}{N_\alpha}\frac{(N_\alpha-1)!(N_\beta-1)!}{N!}\sum_{p=1}^{N_\alpha}\sum_{q=1}^{N_\beta}\int_{\mathbb{R}^3}F(x_p,x_q)|u_{f_p}(x_p,\sigma_p)|^2|u_{f_q}(x_q,\sigma_q)|^2\,dx_p dx_q\\
&=\frac{N!}{N_\alpha!N_\beta!}\frac{(N_\alpha-1)!(N_\beta-1)!}{N!}\sum_{p=1}^{N_\alpha}\sum_{q=1}^{N_\beta}\int_{\mathbb{R}^3}F(x_p,x_q)|u_{f_p}(x_p,\sigma_p)|^2|u_{f_q}(x_q,\sigma_q)|^2\,dx_p\,dx_q\\
&=\frac{1}{N_\alpha N_\beta}\sum_{p=1}^{N_\alpha}\sum_{q=1}^{N_\beta}\int_{\mathbb{R}^3}F(x_p,x_q)|u_{f_p}(x_p,\sigma_p)|^2|u_{f_q}(x_q,\sigma_q)|^2\,dx_p\,dx_q. \qquad \text{(A47)}
\end{aligned}$$

This is the result we wanted. □

Proof of Lemma 3. By expanding the square, we know that

$$\frac{1}{2}\left(\sum_{i=1}^{p}f(x_i)\right)^2-\frac{1}{2}\sum_{i=1}^{p}f(x_i)^2=\mathrm{Re}\sum_{1\le i<j\le p}f(x_i)f(x_j). \qquad \text{(A48)}$$

Multiplying with $|\psi(X)|^2$ and integrating, we have

$$\begin{aligned}
\mathrm{Re}\sum_{1\le i<j\le p}\int_{\mathbb{R}^{3N}}|\psi(X)|^2f(x_i)f(x_j)dX=&\frac{1}{2}\int_{\mathbb{R}^{3N}}|\psi(X)|^2\left(\sum_{i=1}^{p}f(x_i)\right)^2dX\\
&-\frac{1}{2}\int_{\mathbb{R}^{3N}}|\psi(X)|^2\sum_{i=1}^{p}f(x_i)^2dX. \qquad \text{(A49)}
\end{aligned}$$

We use the Schwarz inequality to get a lower bound on the first term in (A49) :

$$\begin{aligned}
&\left|\int_{\mathbb{R}^{3N}}|\psi(X)|^2\left(\sum_{i=1}^{p}f(x_i)\right)dX\right|^2\\
&\le\int_{\mathbb{R}^{3N}}|\psi(X)|^2dX\int_{\mathbb{R}^{3N}}|\psi(X)|^2\left(\sum_{i=1}^{p}f(x_i)\right)^2dX\\
&=\int_{\mathbb{R}^{3N}}|\psi(X)|^2\left(\sum_{i=1}^{p}f(x_i)\right)^2dX. \qquad \text{(A50)}
\end{aligned}$$

Hence,

$$\begin{aligned}
\mathrm{Re}\int_{\mathbb{R}^{3N}}|\psi(X)|^2\sum_{1\le i<j\le p}f(x_i)f(x_j)dX\ge&\frac{1}{2}\left|\int_{\mathbb{R}^{3N}}|\psi(X)|^2\sum_{i=1}^{p}f(x_i)\right|^2\\
&-\frac{1}{2}\int_{\mathbb{R}^{3N}}|\psi(X)|^2\sum_{i=1}^{p}f(x_i)^2dX. \qquad \text{(A51)}
\end{aligned}$$

□

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