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CONVERGENT ITERATIVE METHODS FOR THE HARTREE EIGENPROBLEM (*)

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Abstract. — *This paper develops some new variational principles for the solutions of Hartree eigenproblems and uses these characterizations to describe convergent iterative algorithms for these problems This is done first for helium and then for general atoms and molecules The variational principles involve minimizing separately convex functionals over the product of convex sets By minimizing in different variables at each step, we are led to descent methods where at each step there is a strictly convex problem with a unique solution The resulting sequence is shown to converge to a solution of the Hartree eigenproblem*

Résumé — *Cet article développe de nouveaux principes variationnels pour les valeurs propres du problème de Hartree et les fonctions propres correspondantes Il utilise ces représentations pour déduire des algorithmes itératifs convergents Ceci est fait tout d'abord pour l'hélium puis pour d'autres atomes et molécules Les principes variationnels nécessitent de minimiser séparément des fonctionnelles convexes sur le produit d'ensembles convexes En minimisant dans différentes variables à chaque pas, nous sommes amenés à des méthodes de descente où à chaque pas il y a un problème strictement convexe avec une solution unique On montre que la séquence qui en résulte converge vers une solution du problème d'origine*

1. INTRODUCTION

The Hartree and Hartree-Fock eigenproblems provide quantum mechanical models of atoms and molecules which are more tractable than the full Schrodinger equations for these systems. They have been extensively used for computational modeling since their introduction by Hartree, Fock and Slater [10], [7] and [21] in the early days of quantum theory.

Recently there has been extensive mathematical work on these problems. One of the first rigorous results appeared in 1970 when Reeken [20] used bifurcation theoretic methods to prove existence of solutions for the Hartree

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equations for the Helium atom. Since then Lieb and Simon [13] and [14], and P. L. Lions and coworkers [9], [15]-[16] have developed a comprehensive theory of these equations.

Despite the enormous amount of computations that have been done on these problems, there appear to be few results on the validity of numerical methods for this problem. De Loura [17] has described a method for the Helium atom and proves some convergence results; in particular he showed that if the problem is solved on a family of balls of increasing radii R_n, with R_n increasing to infinity, then the corresponding minimizers converged to the solution of the original problem [17], (Theorem 2.2). In consequence here we shall look at iterative methods for these problems with $\mathbb{R}^3$ replaced by balls of finite radius and with Dirichlet boundary conditions imposed at the boundary.

This paper will develop, and prove the convergence of, some iterative algorithms for approximating solutions of the Hartree eigenproblem restricted to a finite ball. To do this we will introduce some new formulations of the problem. The usual formulation of these problems is similar to Rayleigh's principle for finding eigenvalues and eigenvectors of self-adjoint linear elliptic operators. It involves minimizing a non-convex, quadratic functional on the unit sphere in L^2. Here we shall describe some different variational principles which have the same critical points and which involve minimizing the difference of two convex functions on a convex set. These are detailed in Sections 5 and 6 for the case of helium and in Sections 9 and 10 for the general case.

The methods described in Auchmuty [3] are then used to describe algorithms for finding critical points of these modified variational principles and also for proving convergence of the resulting iterative sequences to solutions of the Hartree eigen-problem. This is done for helium in Section 7 and for the general case in Sections 11 and 12. The helium case involves a scalar unknown wave-function while in the general case the wave functions will be vector-valued. The algorithms described here are different to the original method proposed by Hartree and to those currently used for the computation of these solutions by chemists. The questions of the theoretical convergence of their methods appears to be still open.

2. FORMULATION OF THE PROBLEM

We shall treat the usual quantum mechanical nonrelativistic Coulomb N-body problem modeling N electrons interacting with K static nuclei. The Hamiltonian for this system is

$$H = - \sum_{i=1}^{N} \left(\frac{1}{2} \Delta_i + V(x_i) \right) + \sum_{i<j} |x_i - x_j|^{-1} \tag{2.1}$$

where

$$V(x) = \sum_{k=1}^{K} \frac{z_k}{|x - a^{(k)}|} \tag{2.2}$$

and $x = (x_1, \ldots, x_N)$ with each x_j in $\mathbb{R}^3$. Here each $z_k > 0$, $a^{(k)}$ is in $\mathbb{R}^3$ and we are using appropriate quantum units.

The function $V(x)$ represents the potential at a point x due to the K nuclei of charges $z_1, \ldots, z_K$, at positions $a^{(1)}, \ldots, a^{(K)}$ in space. The last term in (2.1) models the repulsive interaction between pairs of electrons.

Let $L_a^2(\mathbb{R}^{3N})$ be the space of all anti-symmetric, complex valued functions defined on $\mathbb{R}^{3N}$ with the usual L^2-inner product. A function Φ is antisymmetric, if whenever σ is a permutation of $\{1, 2, \ldots, N\}$, then

$$\Phi(x_{\sigma(1)}, \ldots, x_{\sigma(N)}) = (-1)^{|\sigma|} \Phi(x_1, \ldots, x_N) \tag{2.3}$$

where $|\sigma| = \pm 1$ is the signature of σ. This is a closed subspace of $L^2(\mathbb{R}^{3N})$.

The usual problem is to find the eigenvalues and eigenfunctions of H considered as a linear operator on $L_a^2(\mathbb{R}^{3N})$. These are characterized as the extrema of the quadratic form $\mathcal{H} : L_a^2(\mathbb{R}^{3N}) \to \bar{\mathbb{R}}$ defined by

$$\mathcal{H}(\Phi) = \int_{\mathbb{R}^{3N}} \left[\frac{1}{2} |\nabla \Phi(x)|^2 + \right.$$
$$\left. + \sum_{i=1}^{N} \left(-V(x_i) + \sum_{j=i+1}^{N} \frac{1}{|x_i - x_j|} \right) |\Phi(x)|^2 \right] dx \tag{2.4}$$

on the sphere

$$S_a = \left\{ \Phi \in L_a^2(\mathbb{R}^{3N}) : \int_{\mathbb{R}^{3N}} |\Phi(x)|^2 \, dx = 1 \right\}. \tag{2.5}$$

Here $| \ |$ represents the Euclidean norm, $\nabla \Phi(x)$ is the gradient of Φ in $\mathbb{R}^{3N}$ and this functional $\mathcal{H}$ is taken to be $+\infty$ when Φ is not in the Sobolev space $H^1(\mathbb{R}^{3N})$.

The Hartree approximation to this problem ignores the requirement of antisymmetry and assumes that

$$\Phi(x_1, \ldots, x_N) = \prod_{j=1}^{N} \phi_j(x_j) \tag{2.6}$$

with each ϕ_j in $L^2(\mathbb{R}^3)$ obeying

$$\int_{\mathbb{R}^3} |\phi_j(x)|^2 \, dx = 1 . \tag{2.7}$$

Hartree's problem ($\mathcal{H}a$) is to extremize the functional

$$\mathcal{E}(\phi_1, \dots, \phi_N) = \sum_{i=1}^{N} \int_{\mathbb{R}^3} \left[\frac{1}{2} |\nabla \phi_i|^2 - V |\phi_i|^2 \right] dx + \\ + \frac{1}{2} \sum_{i \neq j} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{|\phi_i(x)|^2 |\phi_j(y)|^2}{|x-y|} dx\, dy \quad (2.8)$$

on the set

$$S_N = \{ (\phi_1, \dots, \phi_N) : \phi_j \in H^1(\mathbb{R}^3) \text{ and } \phi_j \text{ obeys (2.7) for } 1 \leq j \leq N \} . \quad (2.9)$$

The value

$$\mathcal{E}_0 = \inf_{\Phi \in S_N} \mathcal{E}(\Phi) \quad (2.10)$$

will be the Hartree estimate of the ground state energy of the problem.

The Euler-Lagrange equations imply that the extrema of (2.8) subject to (2.9) are solutions of

$$-\frac{1}{2} \Delta \phi_i - V \phi_i + \phi_i(x) \sum_{j \neq i} \int \frac{|\phi_j(y)|^2}{|x-y|} dy = \lambda_i \phi_i(x) \quad 1 \leq i \leq N \quad (2.11)$$

on $\mathbb{R}^3$ where $\lambda = (\lambda_1, \dots, \lambda_N)$ are the energy levels corresponding to the eigenstate $\phi_i(x)$, $1 \leq i \leq N$. Mathematically the λ_i are Lagrange multipliers arising from the N constraints of the form (2.7).

For our numerical purpose, we shall restrict attention to the case where $\mathbb{R}^3$ is replaced by the closed ball B_R centered at the origin and of radius R. Thus we shall treat the problem of minimizing $\mathcal{E}(\Phi)$ on S_N, where the domain of the functions is B_R and the integrals in (2.7) and (2.8) are over B_R in place of $\mathbb{R}^3$. This is necessary for our analysis as we will repeatedly use various compact embedding results that require the domain to be bounded. It is justified by the results of de Loura [17]. For actual computation one would expect to choose R sufficiently large that the eigenfunctions of interest obey

$$|\phi_i(x)| < \varepsilon \quad \text{for} \quad |x| \geq R .$$

Specific estimates of R depend on having good decay estimates for the eigenfunctions — such results are not currently known to the authors but would be useful information. Henceforth whenever no domain of integration is indicated, the integrals should be taken over B_R.

In sections 4-7 we shall first describe our methods and results for the

Helium atom. This has $N = 2$, $z_1 = 2$, we can assume $u = \phi_1 = \phi_2$ and

$$V(x) = \frac{2}{|x|}. \tag{2.12}$$

Then the Hartree functional is

$$\mathscr{E}(u) = \int_{B_R} \left[\frac{1}{2} |\nabla u|^2 - \left(V(x) - \frac{1}{2} Q(u^2)(x) \right) u(x)^2 \right] dx \tag{2.13}$$

where

$$Q(w)(x) = \int_{B_R} \frac{w(y)}{|x-y|} dy \tag{2.14}$$

and V is defined by (2.12). The problem $(\mathscr{H}e)$ is to find $\hat{u}$ in

$$\mathscr{S} = \left\{ u \in H_0^1(B_R) : \int_{B_R} |u|^2 \, dx = 1 \right\} \tag{2.15}$$

which minimizes $\mathscr{E}$ on $\mathscr{S}$ and to evaluate the minimal energy

$$\mathscr{E}_0 = \mathscr{E}(\hat{u}) = \inf_{u \in \mathscr{S}} \mathscr{E}(u). \tag{2.16}$$

In this problem $\mathscr{E}$ is a non-convex functional and $\mathscr{S}$ is an unbounded and non-convex set.

3. NOTATION AND MATHEMATICAL BACKGROUND

All the functions used henceforth will be real valued. $\mathbb{R}$ is the set of real numbers and $\bar{\mathbb{R}} = \mathbb{R} \cup \{\pm\infty\}$ is the extended reals. $|\ |$ will denote a Euclidean metric, while $\|\ \|_p$ will denote the L^p-norm. When p is omitted, it should be taken to be 2. The symbol C denotes a constant which need not be the same each time.

We shall use many standard results from functional analysis and the calculus of variations. When a term is used without definition, it should be taken as in Zeidler [23] or Blanchard and Brüning [4].

The Sobolev spaces $H^1(B_R)$ and $H_0^1(B_R)$ are defined in the usual manner with their norms given by

$$\|u\|_{1,2}^2 = \int_{B_R} [|\nabla u|^2 + |u|^2] \, dx.$$

The Sobolev embedding theorems in 3-dimensions say that the embedding $i : H_0^1(B_R) \to L^p(B_R)$ is a continuous linear map when $1 \leq p \leq 6$ and that it is compact when $1 \leq p < 6$. We shall repeatedly use Hardy's inequality (see page 41 of [11]), that

$$\frac{4}{(n-2)^2} \int_\Omega |\nabla u|^2 \, dx \geq \int_\Omega \frac{u^2(y)}{|x-y|^2} \, dy \tag{3.1}$$

whenever Ω is an open set in $\mathbb{R}^n$ and u is in $H^1(\Omega)$.

The space $H_0^1(B_R ; \mathbb{R}^N)$ will denote the Cartesian product of N copies of $H_0^1(B_R)$. Let $\mathcal{S} = \{u \in H_0^1(B_R) : \|u\| = 1\}$ and $\mathcal{S}_N = \mathcal{S} \times \cdots \times \mathcal{S}$ be the Cartesian product of N copies of $\mathcal{S}$. These are the sets defined in (2.15) and (2.9) and are the domains for the Hartree variational principles.

LEMMA 3.1 : *$\mathcal{S}$ is weakly closed in $H_0^1(B_R)$ and $\mathcal{S}_N$ is weakly closed in $H_0^1(B_R ; \mathbb{R}^N)$.*

Proof : Let $\{u_n : n \geq 1\}$ be a weakly convergent sequence in $\mathcal{S}$ which converges weakly to u in $H_0^1(B_R)$. Then u_n converges strongly to u in $L^2(B_R)$ as the embedding is compact. Thus $\|u\| = 1$ and so $\mathcal{S}$ is weakly closed. Similarly in the vector valued case. □

When a sequence $\{u_n : n \geq 1\}$ in a Banach space X converges strongly to a limit u in X we shall write $u_n \to u$. Weak convergence will be written $u_n \rightharpoonup u$.

We shall repeatedly use some Ehrling-type inequalities. Since all the proofs we have seen are via contradiction we will give a constructive proof shown to us by John Froelich [8].

THEOREM 3.1 : *Let X, Y and Z be Banach spaces and i, j be mappings from X to Y and from Y to Z respectively. If i is linear, $1-1$ and compact and j is linear, $1-1$ and continuous then for any $\varepsilon > 0$ there exists a constant $C(\varepsilon)$ such that, for all $u \in X$,*

$$\|i(u)\|_Y \leq \varepsilon \|u\|_X + C(\varepsilon) \|j \circ i(u)\|_Z . \tag{3.2}$$

Proof : In the following proof, $\|u\|_Y$ should be understood as $\|i(u)\|_Y$ and $\|u\|_Z$ should be $\|j \circ i(u)\|_Z$. Assume $\|u\|_X = 1$ first. Let $S = \{u \in Y \mid \|i(u)\|_Y \leq \varepsilon\}$. If $u \in S$ then theorem is true. Let S^c be the complement of S. If $u \in S^c$, we have $\varepsilon < \|u\|_Y$ and the closure of S^c in Y is compact. Consider the function $u \to \|u\|_Z$ for $u \in \bar{S}^c$. It attains a minimum on $\bar{S}^c$ and if this were 0 there would be a $v \in Y$ with $\varepsilon \leq \|v\|_Y$ such that $j(v) = 0$. This contradicts the assumption that j is linear and $1-1$. Hence the mapping $v \to \|v\|_Y / \|v\|_Z$ is a continuous function on

$\bar{S}^c$. It attains a maximum, say $C(\varepsilon)$. i.e. $\|u\|_Y \leq C(\varepsilon)\|u\|_Z$. So for any u with $\|u\|_X = 1$ we have $\|u\|_Y \leq \varepsilon + C(\varepsilon)\|u\|_Z$.

Now for any $u \in X$, we have

$$\left\| \frac{u}{\|u\|_X} \right\|_Y \leq \varepsilon + C(\varepsilon) \left\| \frac{u}{\|u\|_X} \right\|_Z$$

which implies (3.2). □

We shall also repeatedly use certain properties of the Newtonian potential energy functional $\mathcal{Q} : L^p(B_R) \to \bar{\mathbb{R}}$ defined by

$$\mathcal{Q}(f) = \iint \frac{f(x) f(y)}{|x-y|} dx\, dy\,. \tag{3.3}$$

LEMMA 3.2 : *When $p > 6/5$, the functional $\mathcal{Q}$ defined by* (3.3) *is continuous, non-negative and convex. $\mathcal{Q}(f) = 0$ iff $f \equiv 0$.*

Proof : Define

$$Q(f)(x) = \int \frac{f(y)}{|x-y|} dy = \left(\frac{1}{|x|} * f \right)(x) \tag{3.4}$$

where $*$ denotes convolution. From Young's inequality for convolution $Q(f) \in L^\infty(B_R)$ if $p > 3/2$ and $Q(f) \in L^q(B_R)$ for $1 \leq q < 3p/(3-2p)$ when $p \leq 3/2$. This holds as $|x|^{-1}$ is in $L^r(B_R)$ for $1 \leq r < 3$.

Now $\mathcal{Q}(f) = \int f Q(f)\, dx$ where $Q(f)$ is defined by (3.4). Applying Hölder's inequality to this we see that when $p > 6/5$ there is a constant $C(R, p)$ such that

$$\mathcal{Q}(f) \leq C(R, p) \|f\|_p^2\,.$$

This shows that $\mathcal{Q}$ is continuous when $p > 6/5$ as it is a bounded quadratic form on $L^p(B_R)$.

Now $Q(f)(x)$ is the solution of

$$-\Delta u = 4\pi f \tag{3.5}$$

on $\mathbb{R}^3$ which decays to zero as $|x| \to \infty$. Thus

$$\mathcal{Q}(f) = \int_{\mathbb{R}^3} f Q(f)\, dx = -(4\pi)^{-1} \int_{\mathbb{R}^3} u\, \Delta u\, dx$$

when f has support in B_R. Thus

$$4\pi \mathcal{Q}(f) = \int_{\mathbb{R}^3} |\nabla u|^2\, dx \geq 0$$

so $\mathcal{Q}$ is non-negative Since $\mathcal{Q}$ is quadratic in f this implies $\mathcal{Q}$ is convex on $L^p(B_R)$.

$\mathcal{Q}(f) = 0$ if and only if $\nabla u \equiv 0$ on $\mathbb{R}^3$ and thus u is constant on $\mathbb{R}^3$. From (3.5), this can only happen when $f \equiv 0$. □

4. THE HARTREE EIGENPROBLEM FOR HELIUM

In the next two sections we shall prove various results that enable us to develop convergent numerical algorithms for analyzing the problem of the Hartree eigenproblem for the Helium atom. Thus our interest is in analyzing the problem of minimizing $\mathcal{E}$ given by (2.12)-(2.14) on $\mathcal{S}$ defined by (2 15) and to find the minimal value $\mathcal{E}_0$.

The first term in (2.13) is the Dirichlet integral of u and it is a norm on $H_0^1(B_R)$. This determines our choice of the function space for this problem. We shall first prove some results about the other two terms in $\mathcal{E}$. Define I_1, I_2 on $H_0^1(B_R)$ by

$$I_1(u) = \int V(x)\, u(x)^2\, dx \tag{4 1}$$

$$I_2(u) = \iint \frac{u(x)^2\, u(y)^2}{|x-y|}\, dx\, dy\,. \tag{4.2}$$

Here V is a given Lebesgue measurable real-valued function on B_R and we shall often require either

$(V1)$. V is in $L^q(B_R)$ for some $q > 3/2$, and/or

$(V2)$: $V(x) \geq 0$ a.e. on B_R

When either $(V1)$ or $(V2)$ holds, then $I_1(u)$ will be well-defined but possibly infinite In the case of a Helium atom when V is defined by (2.12) both $(V1)$ and $(V2)$ hold as V is in $L^q(B_R)$ for $q < 3$. Similarly for the general potential V defined by (2.2) both $(V1)$ and $(V2)$ hold provided all the nuclei are positively charged.

LEMMA 4.1 · *When V obeys* (V1), *then I_1 defined by* (4.1) *is bounded and weakly continuous on $H_0^1(B_R)$*

Proof When u is in $H_0^1(B_R)$, then u is in $L^p(B_R)$ for $1 \leq p \leq 6$ from the Sobolev embedding theorems Applying Holder's inequality

$$|I_1(u)| \leq \|V\|_q\, \|u\|_r^2 \tag{4.3}$$

where $r = 2\,q/(q-1)$. If $q > 3/2$, then $r < 6$, so I_1 will be bounded on $H_0^1(B_R)$.

Let $\{u_n : n \geq 1\}$ be a sequence which converges weakly to u in $H_0^1(B_R)$. Then u_n converges strongly to u in $L^p(B_R)$ for $1 \leq p < 6$ and

$$\begin{aligned} |I_1(u) - I_1(u_n)| &\leq \int |V| \, \|u^2 - u_n^2\| \, dx \\ &\leq \|V\|_q \, \|u^2 - u_n^2\|_{q^*} \\ &= \|V\|_q \, \|u + u_n\|_r \, \|u - u_n\|_r \end{aligned}$$

where q, q^* are conjugate indices and $r = 2\,q^*$.

When $q > 3/2$, then $q^* < 3$ or $r < 6$ so $I_1(u_n) \to I_1(u)$ as $n \to \infty$ □

LEMMA 4.2 : *Assume V obeys* (V2), *then I_1 defined by* (4.1) *is convex and weakly lower semi-continuous (w.l.s.c.) on $H_0^1(B_R)$.*

Proof : When V obeys $(V2)$ then $I_1(u)$ is well defined and nonnegative for each u in $H_0^1(B_R)$; it may be $+\infty$. Let dom $I_1 = \{u \in H_0^1(B_R) : I_1(u) < \infty\}$, $V_1(x) = \max(1, V(x))$ on B_R, and define $J_1(u) = \int V_1(x)\, u^2(x)\, dx \geq I_1(u)$ for u in $H_0^1(B_R)$. Since $|B_R| < \infty$, u is in dom I_1 implies u is in dom J_1 and by Schwarz's inequality

$$\left(\int V_1\, uw\, dx\right)^2 \leq \int V_1\, u^2\, dx \int V_1\, w^2\, dx = J_1(u)\, J_1(w)$$

for all u, w in dom J_1.

Thus u, $w \in$ dom J_1 implies $(1-t)u + tw$ is in dom J_1 for $0 \leq t \leq 1$ and thus dom I_1 is convex, as dom I_1 = dom J_1.

Given u, w in dom I_1, consider $\varphi(t) = I_1(u + tw) - I_1(u)$. This has $|\varphi'(0)| = \left|\int V(x)\, u(x)\, w(x)\, dx\right| \leq \int |V_1(x)\, \|u(x)\|\, w(x)|\, dx$. So this is finite and $\varphi(t) - \varphi(0) - t\varphi'(0) = t^2 I_1(w) \geq 0$. So φ is convex. Thus I_1 is convex on $H_0^1(B_R)$.

To show that I_1 is weakly l.s.c. on $H_0^1(B_R)$, we first show that $E_c = \{u \in H_0^1(B_R) : I_1(u) \leq c\}$ is closed in $H_0^1(B_R)$ for all c. Let $\{u_n : n \geq 1\}$ be a sequence in E_c with $u_n \to v$ in $H_0^1(B_R)$. Then there is a subsequence $\{u_{n_j}\}$ which converges a.e. to v on B_R. From Fatou's lemma, as V obeys $(V2)$,

$$I_1(v) \leq \liminf_{j \to \infty} I_1(u_{n_j}) \leq c\,.$$

Hence v is in E_c and E_c is closed. But E_c is convex, so it is weakly closed and thus I_1 is weakly l.s.c. on $H_0^1(B_R)$. □

LEMMA 4.3 : *The functional I_2 defined by* (4.2) *is non-negative, bounded, convex and weakly continuous on $H_0^1(B_R)$.*

Proof Note that $I_2 = \mathcal{Q}(u^2)$ where $\mathcal{Q}$ is defined by (3.3). Thus Lemma 3.3 and the Sobolev embedding theorem implies that I_2 is bounded and non-negative.

If $\{u_n : n \geq 1\}$ is a sequence in $H_0^1(B_R)$ which converges weakly to u, then u_n^2 converges strongly to u^2 in $L^r(B_R)$ for $1 \leq r < 3$. Hence from Lemma 3.2, $I_2(u) = \mathcal{Q}(u^2) = \lim_{n \to \infty} \mathcal{Q}(u_n^2)$ so I_2 is weakly continuous.

When u, w are in $H_0^1(B_R)$, define $\varphi(t) = I_2(u + tw)$ Then φ is a quartic polynomial and

$$\varphi''(0) = 4 \iint \frac{u^2(x)\, w^2(y)}{|x - y|}\, dx\, dy + 8 \iint \frac{u(x)\, w(x)\, u(y)\, w(y)}{|x - y|}\, dx\, dy .$$

The first term here is non-negative as the integrand is non-negative, while the second term is non-negative upon taking $f = uw$ and using Lemma 3.2. Since u, w are arbitrary in $H_0^1(B_R)$ this shows that I_2 is convex. □

A functional f on a Banach space X is said to be coercive if

$$\lim_{\|x\| \to \infty} \frac{f(x)}{\|x\|} = \infty .$$

We are now in a position to show that $\mathcal{E}$ is coercive on $H_0^1(B_R)$ and this will enable the proof of existence results.

LEMMA 4.4 : *Assume V obeys* ($V1$), *then $\mathcal{E}$ is coercive on $H_0^1(B_R)$.*

Proof To prove this we need a lower bound on $I_2(u)$ and a upper bound on $I_1(u)$. First observe the elementary inequality, $Q(u^2)\,(x) \geq \frac{1}{2R}\, \|u\|^2$, so

$$I_2(u) = \int u^2\, Q(u^2) \geq \frac{1}{2R}\, \|u\|^4 .$$

When V is in $L^q(B_R)$ for some $q > 3/2$, then (4.3) holds with $r = 2q/(q-1) > 2$. Take $X = H_0^1(B_R)$, $Y = L^r(B_R)$ and $Z = L^2(B_R)$ in Theorem 3.1. Then for each $\varepsilon > 0$, there is a $C(\varepsilon) > 0$ such that

$$\|u\|_r \leq \varepsilon\, \|\nabla u\| + C(\varepsilon)\, \|u\|$$

or

$$\|u\|_r^2 \leq 2\, \varepsilon^2\, \|\nabla u\| + 2\, C(\varepsilon)^2\, \|u\|^2 .$$

Using these results and (4.3) in (2.13), we see that

$$\mathcal{E}(v) \geq (1 - 2\, \varepsilon^2\, \|V\|_q)\, \|\nabla u\|^2 + \frac{1}{2R}\, \|u\|^4 - 2\, C_1\, \|V\|_q\, \|u\|^2 . \quad (4.4)$$

Choose $\varepsilon^2 = \dfrac{1}{4\,\|V\|_q}$, then

$$\mathscr{E}(v) \geq \frac{1}{2}\,\|\nabla u\|^2 + \frac{1}{2R}\,(\|u\|^2 - 2\,C_2\,\|V\|_q)^2 - C_3$$

where C_1, C_2, C_3 are constants This right hand side is coercive on $H_0^1(B_R)$ so $\mathscr{E}$ also is □

THEOREM 4 1 *When V obeys $(V1)$ there is a $\hat{u}$ in $\mathscr{S}$ which minimizes $\mathscr{E}$ on $\mathscr{S}$ and $\mathscr{E}(\hat{u})$ is finite*

Proof From Lemma 3 1, $\mathscr{S}$ is weakly closed in the reflexive Banach space $H_0^1(B_R)$ $\mathscr{E}$ is weakly l s c on $H_0^1(B_R)$ since I_1, I_2 are weakly continuous and the first term in $\mathscr{E}$ is a norm on $H_0^1(B_R)$ It is coercive on $H_0^1(B_R)$ and thus on $\mathscr{S}$ from Lemma 4 4 Hence by corollary 38 14 of [23], $\mathscr{E}$ attains its infimum on $\mathscr{S}$ and $\mathscr{E}(\hat{u})$ is finite □

Now we shall show that the minimizers of $\mathscr{E}$ on $\mathscr{S}$ are non-trivial solutions of the usual Hartree eigenvalue problem

$$-\frac{1}{2}\,\Delta\, u(x) - V(x)\, u(x) + u(x) \int \frac{u^2(y)\, dy}{|x-y|} = \lambda\, u(x) \quad \text{in} \quad B_R \qquad (4\ 5)$$

with u in $H_0^1(B_R)$ and

$$\int u^2\, dx = 1 \qquad (4\ 6)$$

LEMMA 4 5 *Assume V obeys $(V1)$, then $\mathscr{E}$ is Gateaux differentiable at each u in $H_0^1(B_R)$ and the G-derivative of $\mathscr{E}$ at u is*

$$\mathscr{E}'(u) = -\,\Delta u - 2\,Vu + 2\,uQ\,(u^2) \qquad (4\ 7)$$

Proof Let $\varphi(t) = \mathscr{E}(u + th)$, where u, h are in $H_0^1(B_R)$ The Gateaux derivative of $\mathscr{E}$ at u is the element v of $H^{-1}(B_R)$ such that $\varphi'(0) = \langle v, h\rangle$ for all h in $H_0^1(B_R)$ Here $\langle , \rangle$ is the usual pairing of $H_0^1(B_R)$ and its dual space $H^{\ 1}(B_R)$ through $L^2(B_R)$

Now $\varphi_1(t) = I_1(u + th)$ has

$$\varphi_1'(0) = 2 \int V(x)\, u(x)\, h(x)\, dx$$

and provided V obeys (V1), then $Vu \in L^p(B_R)$ for $p > 6/5$ or $Vu \in H^{-1}(B_R)$

Similarly $\varphi_2(t) = I_2(u + th)$ has

$$\phi_2'(0) = 4 \int u(x)\, h(x)\, Q\,(u^2)\, dx$$

upon using the symmetry of Q and Fubini's theorem When u is in $H_0^1(B_R)$, $Q(u^2)$ is in $L^\infty(B_R)$ (as in proof of Lemma 3 2) and thus $uQ(u^2)$ will be in $L^6(B_R)$

The proof that the Dirichlet integral is G-differentiable on $H_0^1(B_R)$ and the derivative is $-2\,\Delta u$ is standard, so (4 7) follows □

THEOREM 4 2 *When V obeys $(V1)$ and $\hat{u}$ minimizes $\mathscr{E}$* on $\mathscr{S}$, *then $\hat{u}$ is a (weak) solution of* (4 5)-(4 6) *and*

$$\mathscr{E}(\hat{u}) + \frac{1}{2} I_2(\hat{u}) = \lambda \tag{4 8}$$

Proof The problem $(\mathscr{H}e)$ of minimizing $\mathscr{E}$ on $\mathscr{S}$ is a constrained minimization problem where the constraint is (4 6) The Lagrange multiplier principle applies as in propositions 43 19 and 43 21 of [23], so the minimizer $\hat{u}$ obeys

$$\mathscr{E}'(u) = 2\,\lambda u \tag{4 9}$$

for some real λ Substituting (4 7) here we obtain (4 5)

Multiply (4 5) by $\hat{u}$, integrate and use the divergence theorem, then $\hat{u}$ obeys

$$\frac{1}{2}\int |\nabla u|^2\,dx - \int V u^2\,dx + \iint \frac{u^2(x)\,u^2(y)}{|x-y|}\,dx\,dy = \lambda$$

as (4 6) holds This and the definition (2 13) of $\mathscr{E}$ implies (4 8) □

In general a function u in $\mathscr{S}$ is said to be a critical point of $\mathscr{E}$ on $\mathscr{S}$ provided it is a solution of (4 9) for some λ These will define the eigenstates of the Hartree problem for Helium

In this proof (4 9) is an equality of elements of $H^{-1}(B_R)$ Since $\hat{u}$ is in $H_0^1(B_R)$, (4 5) implies that

$$-\Delta u = (V + \lambda)\,u - uQ(u^2)$$

and this right hand side is at least in $L^{6/5}(B_R)$ when V obeys (V1) Hence $\hat{u}$ is actually in $W^{2\ 6/5}(B_R)$ Under more regularity conditions on V, we can obtain better regularity of the solution of (4 5)-(4 6)

THEOREM 4 3 *Assume V is given by* (2 12) *and $\hat{u}$ is a solution in $H_0^1(B_R)$ of* (4 5)-(4 6) *Then $\hat{u}$ is in $W^{2\ r}(B_R)$ for $1 \le r < 3$, it is in $C^\alpha(B_R)$ for $0 < \alpha < 1$ and it is in $W^{1\ p}(B_R)$ for all $1 \le p < \infty$*

Proof When V is defined by (2 12), V is in $L^p(B_R)$ for $1 \le p < 3$ When $\hat{u}$ is in $H_0^1(B_R)$, from the Sobolev theorem it is in $L^6(B_R)$ and thus $V\hat{u}$ is in $L^r(B_R)$ for $1 \le r < 2$

From equation (4.5), $\hat{u}$ obeys an equation of the from

$$- \Delta u = f \tag{4.10}$$

with f in L^r for $1 \leq r < 2$, so u is in $W^{2,r}(B_R)$ for $1 \leq r < 2$.

This implies $\hat{u}$ is in $L^\infty(B_R)$ from Sobolev and thus f in (4.10) is actually in L^r for $1 \leq r < 3$. So $\hat{u}$ is in $W^{2,r}(B_R)$ for $1 \leq r < 3$. Applying the Sobolev theorem to this, the last two parts of this theorem follow. □

5. MODIFIED VARIATIONAL PRINCIPLE FOR HELIUM

The variational principle $(\mathscr{H}e)$ has the standard Rayleigh form for eigenvalue problems. It involves minimizing a non-convex functional on a non-convex set and consequently there are considerable difficulties in proving that algorithms for minimizing $\mathscr{E}$ on $\mathscr{S}$ converge. Here we shall introduce and analyze some modified variational principles for which it is easier to describe the convergence of iterative algorithms.

First we shall look at the Schroedinger eigenproblem associated with the linear part of (4.5). Assume V obeys $(V1)$ and define $\mathscr{H}_V : H_0^1(B_R) \to \mathbb{R}$ by

$$\mathscr{H}_V(u) = \int \left[\frac{1}{2} |\nabla u|^2 - V |u|^2 \right] dx . \tag{5.1}$$

Consider the problem $(\mathscr{D}_V)$ of minimizing $\mathscr{H}_V$ on $\mathscr{S}$ and finding

$$\lambda_1(V) = \inf_{u \in \mathscr{S}} \mathscr{H}_V(u) \tag{5.2}$$

$\lambda_1(V)$ is the ground-state energy associated with the potential V.

THEOREM 5.1 : *Assume* $(V1)$ *holds and* $\mathscr{H}_V$, λ_1 *are defined by* (5.1)-(5.2), *then* $\lambda_1(V)$ *is finite.*

Proof : $\mathscr{H}_V$ only involves the first two terms of $\mathscr{E}$, so we can repeat the estimates in the proof of Lemma 4.4 to obtain an analog of (4.4). Namely

$$\mathscr{H}_V(u) \geq (1 - 2\,\varepsilon^2 \|V\|_q) \|\nabla u\|^2 - C_1 \|V\|_q \|u\|^2 .$$

Choose ε sufficiently small, then this implies

$$\lambda_1 \geq - C_1 \|V\|_q$$

as $\|u\| = 1$ on $\mathscr{S}$. Hence λ_1 is finite.

For the particular case of the Coulomb field with

$$V(x) = \frac{z}{|x|}$$

a classical analysis, shows that $\lambda_1 \geqslant - z^2/4$ (compare [12], § 36), so for the Helium atom $\lambda_1 \geqslant -1$

Our modified variational principle ($\mathscr{P}\mathscr{H}e$) for finding the ground state of the Helium atom will be based on minimizing the functional $\mathscr{F}_\eta$ $H_0^1(B_R) \to \mathbb{R}$ defined by

$$\mathscr{F}_\eta = \mathscr{E}(u) - \frac{\eta}{2} \|u\|^2 \tag{5 3}$$

on the ball

$$\mathscr{B} = \left\{ u \in H_0^1(B_R) \quad \int u^2 \, dx \leqslant 1 \right\} \tag{5 4}$$

We shall show that, when η is sufficiently large, the minimizers of $\mathscr{F}_\eta$ on $\mathscr{B}$ will also minimize $\mathscr{E}$ on $\mathscr{S}$ This problem has the advantage that the domain $\mathscr{B}$ is a closed convex set in $H_0^1(B_R)$

THEOREM 5 2 *Assume (V1) holds, then there is a $\hat{u}_\eta$ in $\mathscr{B}$ which minimizes $\mathscr{F}_\eta$ on $\mathscr{B}$ It obeys*

$$\mathscr{E}'(u) - \eta u = \mu u \tag{5 5}$$

for some real μ If $\|\hat{u}_\eta\| < 1$ then $\mu = 0$ while if $\mu \neq 0$, then $\|\hat{u}_\eta\| = 1$

Proof The embedding of $H_0^1(B_R)$ into $L^2(B_R)$ is compact from Rellich's theorem so the functional $\|u\|^2$ is weakly continuous on $H_0^1(B_R)$ Since $\mathscr{E}$ is w l s c and coercive on $\mathscr{B}$, so also is $\mathscr{F}_\eta$ $\mathscr{B}$ is a closed, convex set in $H_0^1(B_R)$ so it is weakly closed and thus $\mathscr{F}_\eta$ attains its infimum on $\mathscr{B}$

$\mathscr{F}_\eta$ is G-differentiable on $H_0^1(B_R)$ with

$$\mathscr{F}_\eta(u) = \mathscr{E}'(u) - \eta u$$

since $\mathscr{E}$ is Thus the minimizer $\hat{u}_\eta$ of $\mathscr{F}_\eta$ on $\mathscr{B}$ obeys

$$\langle \mathscr{F}_\eta'(u), h \rangle \geqslant 0$$

for all h in $H_0^1(B_R)$ such that $\hat{u}_\eta + th$ is in $\mathscr{B}$ for all sufficiently small positive t

If $\|\hat{u}_\eta\| < 1$, this implies $\mathscr{F}_\eta'(u) = 0$ or (5 5) holds with $\mu = 0$

If $\|\hat{u}_\eta\| = 1$, then h must obey $\langle \hat{u}_\eta, h \rangle \leqslant 0$ and then there is a $\mu \leqslant 0$ such that $\hat{u}_\eta$ obeys (5 5) In particular if $\hat{u}_\eta$ obeys (5 5) with $\mu \neq 0$, then $\|\hat{u}_\eta\| = 1$ □

Suppose $\hat{u}_\eta$ is defined as in Theorem 5 2 Multiplying (5 5) by $\hat{u}_\eta$ and integrating over B_R leads to

$$\mathscr{E}(\hat{u}_\eta) + \frac{1}{2} I_2(\hat{u}_\eta) = (\mu + \eta) \|\hat{u}_\eta\|^2 \tag{5 6}$$

From the definition of $\hat{u}$ and $\mathscr{E}_0$ we have

$$\mathscr{E}(\hat{u}_\eta) - \frac{\eta}{2} \|\hat{u}_\eta\|^2 \leq \inf_{u \in \mathscr{S}} \mathscr{F}_\eta(u) = \mathscr{E}_0 - \frac{\eta}{2}$$

so
$$2\,\mathscr{E}(\hat{u}_\eta) \leq 2\,\mathscr{E}_0 + \eta(\|\hat{u}_\eta\|^2 - 1)$$

When $\lambda_1 = \lambda_1(V)$ is defined by (5 2), then

$$\mathscr{E}(\hat{u}_\eta) \geq \lambda_1 \|\hat{u}_\eta\|^2 + \frac{1}{2} I_2(\hat{u}_\eta)$$

so
$$2\,\mathscr{E}(\hat{u}_\eta) \geq (\lambda_1 + \mu + \eta) \|\hat{u}_\eta\|^2 \tag{5 7}$$

upon adding (5 6) to this inequality Combine with (5 7) then

$$(\lambda_1 + \mu) \|\hat{u}_\eta\|^2 \leq 2\,\mathscr{E}_0 - \eta \tag{5 8}$$

Define

$$\eta_c = \begin{cases} 2\,\mathscr{E}_0 & \text{if } \lambda_1(V) \geq 0 \\ 2\,\mathscr{E}_0 - \lambda_1 & \text{if } \lambda_1(V) < 0 \end{cases} \tag{5 9}$$

then (5 8) implies that

$$\mu \|\hat{u}_\eta\|^2 \leq 2\,\mathscr{E}_0 - \eta - \lambda_1 \|\hat{u}_\eta\|^2 \leq -(\eta - \eta_c)$$

When $\eta > \eta_c$ then $\mu < 0$ and so $\|\hat{u}_\eta\|^2 = 1$ from Theorem 5 2

THEOREM 5 3 *Assume* $(V1)$ *holds,* η_c *is defined by* (5 9) *and* $\eta > \eta_c$ *If* u_η *minimize* $\mathscr{F}_\eta$ *on* $\mathscr{B}$, then $u_\eta = u$ minimizes $\mathscr{E}$ *on* $\mathscr{S}$ *and is a solution of* $(\mathscr{H}e)$

Proof We have shown above that when $\eta > \eta_c$ we must have $\|\hat{u}_\eta\| = 1$ Hence $\hat{u}_\eta$ must minimize $\mathscr{E}$ on $\mathscr{S}$, since it minimizes $\mathscr{F}_\eta = \mathscr{E}(u) - \eta/2$ on $\mathscr{S}$ Thus the result follows □

6 SEPARATELY CONVEX VARIATIONAL PRINCIPLE

In this section, methods from non-convex duality theory as described in Auchmuty [2] and [3], will be used to develop yet another class of variational principles whose solutions yield eigenfunctions of the Hartree eigenproblem

The variational principle to be described here involves a functional defined on a product of two convex sets which is convex and lower semi-continuous in each variable separately

The theories in [2] and [3] described duality theories for variational principles which involve the minimization of the difference of two convex functionals The functional $\mathscr{F}_\eta$ defined by (5 3) may be written as

$$\mathscr{F}_\eta(u) = f_1(u) - f_2(u, \eta) \tag{6 1}$$

where

$$2 f_1(u) = \int |\nabla u|^2 \, dx + I_2(u) \tag{6 2}$$

and

$$f_2(u, \eta) = \int (V(x) + \eta) \, u^2(x) \, dx \tag{6 3}$$

The properties of the Dirichlet integral and Lemma 4 3 imply that f_1 is convex and weakly l s c on $H_0^1(B_R)$ When $\eta > 0$ and V obeys (V2), then Lemma 4 2 shows that $f_2(., \eta)$ is also convex and weakly l s c on $H_0^1(B_R)$ so (6 1) is a decomposition of $\mathscr{F}_\eta$ into the difference of two convex functionals

For certain technical reasons, it is more convenient to regard $f_2(., \eta)$ as being defined on $L^6(B_R)$ In this case it has the following properties

LEMMA 6 1 *Assume V obeys* (V1) *and* (V2) *and* $f_2 \; L^6(B_R) \times (0, \infty) \to [0, \infty]$ *is defined by* (6 3) *Then $f_2(\,.\,, \eta)$ is (weakly) l s c and convex and its convex conjugate functional* $f_2^*(\,.\,, \eta) \; L^{6/5}(B_R) \times (0, \infty) \to [0, \infty]$ *is given by*

$$f_2^*(w, \eta) = \frac{1}{4} \int \frac{w^2(x)}{\eta + V(x)} \, dx \tag{6 4}$$

f_2^* is nonnegative, convex and l s c on $L^{6/5}(B_R)$

Proof The proof that $f_2(., \eta)$ is (weakly) l s c and convex on $L^6(B_R)$ is essentially the same as the proof of Lemma 4 3

The conjugate convex functional $f_2^*(w, \eta)$ is defined by

$$f_2^*(w, \eta) = \sup_{u \in L^2(B_R)} \int [uw - (V(x) + \eta) \, u^2] \, dx$$
$$= \frac{1}{4} \int \frac{w^2(x)}{\eta + V(x)} \, dx$$

upon using proposition 2 2, chapter IX of Ekeland & Temam [5] Since $f_2^*(., \eta)$ is the supremum of a family of convex and l s c functionals on $L^{6/5}(B_R)$, it is again convex and l s c

Consider the functional $\mathscr{L} : H_0^1(B_R) \times L^{6/5}(B_R) \times (0, \infty) \to \bar{\mathbb{R}}$ defined by

$$\mathscr{L}(u, w ; \eta) = f_1(u) + f_2^*(w, \eta) - \int uw \tag{6.5}$$

$$= \int \left[\frac{1}{2} |\nabla u|^2 - uw + \frac{1}{2} u^2(x) \int \frac{u^2(y)\, dy}{|x-y|} + \frac{1}{4} \frac{w^2(x)}{\eta + V(x)} \right] dx \tag{6.6}$$

and consider the problem $(\mathscr{Q}_\eta)$ of minimizing $\mathscr{L}(., . ; \eta)$ on $\mathscr{B} \times L^{6/5}(B_R)$ and finding

$$\alpha(\eta) = \inf_{u \in \mathscr{B}} \inf_{w \in L^{6/5}(B_R)} \mathscr{L}(u, w ; \eta). \tag{6.7}$$

LEMMA 6.2 : *Assume V obeys (V1) and (V2) and $\eta > 0$. Then*
(i) *for each w in $L^2(B_R)$, $\mathscr{L}(., w ; \eta)$ is coercive, strictly convex and weakly lower semi-continuous on $\mathscr{B}$,*
(ii) *for each u in $\mathscr{B}$, $\mathscr{L}(u, . ; \eta)$ is convex and l.s.c. on $L^{6/5}(B_R)$ and there is a unique $\hat{w}(u, \eta)$ in $L^{6/5}(B_R)$ which minimizes $\mathscr{L}(u, . ; \eta)$ on $L^{6/5}(B_R)$. Moreover*

$$\mathscr{F}_\eta(u) = \inf_{w \in L^{6/5}(B_R)} \mathscr{L}(u, w ; \eta). \tag{6.8}$$

Proof : (i) When u is in $\mathscr{B}$, u is in $L^6(B_R)$ so $\int uw\,dx$ is a continuous linear functional on $H_0^1(B_R)$ for each w in $L^{6/5}(B_R)$. Using Lemma 4.3, $\mathscr{L}(., w ; \eta)$ is seen to be the sum of two weakly continuous, convex functionals and a term which is strictly convex, weakly l.s.c. and coercive. Thus (i) follows.

Moreover $\left| \int uw \right| \leq \|w\|_{6/5} \|u\|_6 \leq C \|w\|_{6/5} \|\nabla u\|$ so $\mathscr{L}(., w ; \eta)$ is coercive on $H_0^1(B_R)$ and on $\mathscr{B}$.

(ii) For each u is in $H_0^1(B_R)$, $\int uw\,dx$ is a continuous linear functional on $L^{6/5}(B_R)$, so together with Lemma 6.1, $\mathscr{L}(u, ., \eta)$ is convex and l.s.c. on $L^{6/5}(B_R)$.

Considered as a function of w, the integrand in (6.6) is minimized pointwise if

$$w(x) = 2(V(x) + \eta)\, u(x) \quad \text{a.e. on } B_R. \tag{6.9}$$

When u is in $\mathscr{B}$ and V obeys (V1), then this right hand side is in $L^{6/5}(B_R)$ from Hölder's inequality. Hence this minimum is attained. It is unique as this functional is strictly convex in w.

Substituting (6 9) in (6 6), we find that (6 8) holds □

This result implies that minimizing $\mathcal{L}(\,.\,,\,.\,,\eta)$ on $\mathcal{B} \times L^{6/5}(B_R)$ is equivalent to minimizing $\mathcal{F}_n$ on $\mathcal{B}$, or the problem $(\mathcal{Q}_\eta)$ is equivalent to $(\mathcal{P}\mathcal{H}e)$

It is worth noting that when w is fixed in $L^{6/5}(B_R)$, the problem of minimizing $\mathcal{L}(\,.\,,w\,,\eta)$ for u in $\mathcal{B}$ has a unique solution $\hat{u}(w,\eta)$ and $\hat{u}$ is a solution of

$$-\frac{1}{2}\Delta u + u(x)\int \frac{u^2(y)}{|x-y|}\,dy = \frac{w}{2} + \lambda u \quad \text{in } B_R \tag{6 10}$$

which also obeys (4 6) The proof is just as Theorem 4 2 Thus if $(\tilde{u},\tilde{w})$ is a local minimizer of $\mathcal{L}(\,.\,,\,.\,,\eta)$ on $H_0^1(B_R)\times L^2(B_R)$, then $\tilde{u}$, $\tilde{w}$ are solutions of (6 9) and (6 10), so $\tilde{u}$ obeys

$$-\frac{1}{2}\Delta u - V(x)\,u + u(x)\int \frac{u^2(y)}{|x-y|}\,dy = (\lambda+\eta)\,u \quad \text{on } \mathcal{B}_R \tag{6 11}$$

subject to (4 6), that is, $\tilde{u}$ will be a solution of the Hartree eigenproblem for Helium

Note also that $\alpha(\eta)$ is finite and there exists a global minimizer $(\tilde{u}_\eta,\tilde{w}_\eta,\eta)$ on $\mathcal{B}\times L^{6/5}(B_R)$ as there is a minimizer of $\mathcal{F}_\eta$ on $\mathcal{B}$ from Theorem 5 2 When $\eta > \eta_c$, Theorem 5 3 shows that $\hat{u}_\eta$ will also minimize the Hartree functional on $\mathcal{S}$

7 ITERATIVE METHOD FOR THE HELIUM EIGENPROBLEM

The variational principle $(\mathcal{Q}_\eta)$ for finding solutions of the Hartree eigenproblem involves the minimization of a functional which is separately strictly convex in each of u, w and defined on the product of two convex sets

A straight forward way to generate a descent sequence for $\mathcal{L}(\,.\,,\,.\,,\eta)$ is to minimize $\mathcal{L}$ in each variable separately Then each step involves solving a strictly convex problem which has a unique solution Since we have the explicit formula (6 9) for minimizing with respect to w, this procedure can be described as follows

ALGORITHM 7 1 1 *Choose* $\eta > 0$, $u^{(0)}$ *in* $\mathcal{B}$ *and define*

$$w^{(0)} = 2(V(x)+\eta)\,u^{(0)} \tag{7 1}$$

2 *For* $k \geq 1$, *find* $u^{(k)}$ *in* $\mathcal{B}$ *such that*

$$\mathcal{L}(u^{(k)}, w^{(k-1)}, \eta) = \inf_{u\in\mathcal{B}} \mathcal{L}(u, w^{(k-1)}, \eta) \tag{7 2}$$

3 *Define*

$$w^{(k)} = 2(V(x) + \eta)\, u^{(k)} \tag{7 3}$$

$$r^{(k)} = -\Delta u^{(k)} + u^{(k)} Q(u^{(k)^2}) - \frac{1}{2} w^{(k)} \tag{7 4}$$

4 *Evaluate*

$$\rho_k = \| r^{(k)} - \langle r^{(k)}, u^{(k)} \rangle\, u^{(k)} \| \tag{7 5}$$

5 If $\rho_k \leqslant \varepsilon$ *stop , else put* $k = k + 1$ *and go to* 2

It is worthwhile to point out some features of this algorithm First note that (7 3) implies that

$$\mathscr{L}(u^{(k)}, w^{(k)}, \eta) = \inf_{w \in L^{6/5}(B_R)} \mathscr{L}(u^{(k)}, w, \eta) \tag{7 6}$$

$$= \mathscr{F}_\eta(u^{(k)}) \quad \text{from (6 8)}$$

The solution $u^{(k)}$ of (7 2) is a solution in $\mathscr{B}$ of

$$-\Delta u + uQ(u^2) = \frac{1}{2} w^{(k-1)} + \lambda_k u \tag{7 7}$$

where λ_k is a multiplier from (6 10) If $w^{(k)} = w^{(k-1)}$, then $u^{(k)}$ will in fact be a solution of the Hartree eigenproblem Otherwise, by strict convexity in w we have

$$\begin{aligned} \mathscr{F}_\eta(u^{(k)}) &= \mathscr{L}(u^{(k)}, w^{(k)}, \eta) < \mathscr{L}(u^{(k)}, w^{(k-1)}, \eta) \\ &= \inf_{u \in \mathscr{B}} \mathscr{L}(u, w^{(k-1)}, \eta) \\ &\leqslant \mathscr{L}(u^{(k-1)}, w^{(k-1)}, \eta) = \mathscr{F}_\eta(u^{(k-1)}) \end{aligned}$$

Moreover strict convexity in u implies that inequality holds on the last line unless $u^{(k)} = u^{(k-1)}$

Thus $\mathscr{F}_\eta(u^{(k)}) < \mathscr{F}_\eta(u^{(k-1)})$ unless $u^{(k-1)} = u^{(k)}$ and $w^{(k-1)} = w^{(k)}$ and in this case we have a solution of the Hartree eigenproblem

To help analyze this theorem, define functionals $h_1 : H_0^1(B_R) \to [0, \infty]$ and $h_2 \; L^p(B_R) \to [0, \infty]$ for $6/5 \leqslant p < 2$ by

$$h_1(u) = \begin{cases} f_1(u) & \text{if } u \in \mathscr{B} \\ \infty & \text{otherwise} \end{cases}$$

and $\qquad h_2(w) = f_2^*(w, \eta) \quad \text{when} \quad w \in L^p(B_R),\ 6/5 \leqslant p < 2$

Both h_1, h_2 are convex, weakly l s c functionals on their domains Then

(7.2) and (7.3) may be written as, given $w^{(k-1)}$, find $u^{(k)} \in \mathscr{B}$ obeying

$$w^{(k-1)} \in \partial h_1(u^{(k)}), \tag{7.8}$$

then find $w^{(k)}$ in $L^p(B_R)$ obeying

$$u^{(k)} \in \partial h_2(w^{(k)}). \tag{7.9}$$

THEOREM 7.1 : *Choose* $\eta > 0$, $u^{(0)}$ *in* $\mathscr{B}$ *and define* V *by* (2.12). *Let* $\Gamma = \{u^{(k)} : k \geq 0\}$ *be the sequence generated by algorithm* 7.1 *with* $\varepsilon = 0$. *Then either*
(i) Γ *is finite and the last term is a solution of the eigenproblem* (6.11), *or*
(ii) Γ *is an infinite, bounded sequence in* $\mathscr{B}$ *which is a strict descent sequence for* $\mathscr{F}_\eta$ *and has at least one weak limit point in* $\mathscr{B}$. *Each weak limit point is a strong limit point and is a solution of the eigenproblem* (6.11).

Proof : (i) was proven above, so we shall consider the case where Γ is infinite. The sequence $\{\mathscr{F}_\eta(u^{(k)}) : k \geq 1\}$ is strictly decreasing and bounded below ; let

$$\alpha(\eta) = \inf_{k \geq 1} \mathscr{F}_\eta(u^{(k)}). \tag{7.10}$$

Since $\mathscr{F}_\eta$ is coercive on $\mathscr{B}$, Γ will be bounded in $\mathscr{B}$. Thus Γ has a weak limit point $\hat{u}$ as $\mathscr{B}$ is a weakly closed, convex set in the reflexive Banach space $H_0^1(B_R)$.

Let $\{u^{(k_j)} : j \geq 1\}$ be a subsequence of Γ converging weakly to $\hat{u}$ in $\mathscr{B}$. Then $u^{(k_j)} \to \hat{u}$ in $L^p(B_R)$ for $p < 6$ from the Sobolev embedding theorem and (7.3) implies that $w^{(k_j)} \to \hat{w}$ in $L^r(B_R)$ for $r < 2$ as V is in $L^q(B_R)$ for $q < 3$.

When u_1, u_2 are in $\mathscr{B}$, $w_1 \in \partial h_1(u_1)$, $w_2 \in \partial h_1(u_2)$, then

$$\langle w_1 - w_2, u_1 - u_2 \rangle \geq \int |\nabla(u_1 - u_2)|^2 \, dx$$

upon using the definition of h_1. Apply Hölder's inequality and the Sobolev embedding theorem here to find that for each $r \geq 6/5$ there is a $C(r)$ such that

$$\|u_1 - u_2\|_{1,2} \leq C(r)^{-1} \|w_1 - w_2\|_r. \tag{7.11}$$

Since $w^{(k_j)} \to \hat{w}$ in $L^r(B_R)$ for $r < 2$, (7.8) and this imply that $u^{(k_j+1)}$ converges strongly to a limit $\tilde{u}$ in $\mathscr{B}$ where $\tilde{u}$ obeys

$$\hat{w} \in \partial h_1(\tilde{u}). \tag{7.12}$$

By replacing $w^{(k_j)}$ with $w^{(k_j - 1)}$ in the above argument we see that $u^{(k_j)}$ converges strongly to $\hat{u}$ in $\mathscr{B}$.

Since h_2 is weakly l.s.c. and convex on $L^r(B_R)$, $6/5 \leq r < 2$, ∂h_2 has a maximal monotone graph from Theorem 47.F in [23] and this graph is weakly-strongly closed as in proposition 3, chapter 6, section 7 of [1]. Thus taking limits in (7.9) we find that

$$\hat{u} \in \partial h_2(\hat{w}) \tag{7.13}$$

and

$$\begin{aligned} \mathscr{F}_\eta(\hat{u}) &= \mathscr{L}(\hat{u}, \hat{w}\,;\eta) && \text{from (6.8)} \\ &\geq \mathscr{L}(\tilde{u}, \hat{w}\,;\eta) && \text{from (7.12)} \\ &\geq \mathscr{F}_\eta(\tilde{u}) \end{aligned}$$

with inequality here unless $\tilde{u} = \hat{u}$.

If $\tilde{u} = \hat{u}$, then (7.12) and (7.13) imply that $\hat{u}$ is a solution of the Hartree eigenproblem.

If $\tilde{u} \neq \hat{u}$, then $\mathscr{F}_\eta(\tilde{u}) < \mathscr{F}_\eta(\hat{u})$. $\mathscr{F}_\eta$ is continuous on $\mathscr{B}$ and $u^{(k_j)}$ converges strongly to $\hat{u}$, so (7.10) implies that

$$\alpha(\eta) = \mathscr{F}_\eta(\hat{u}) > \mathscr{F}_\eta(\tilde{u}) .$$

Since $\mathscr{F}_n(\tilde{u}) = \lim_{j \to \infty} \mathscr{F}_\eta(u^{(k_j + 1)})$ this is impossible so we must have $\tilde{u} = \hat{u}$ and then $\hat{u}$ is a solution of the Hartree eigenproblem. □

8. ANALYSIS OF N-ELECTRON HARTREE EIGENPROBLEM

We shall now extend the preceding analysis of the Hartree approximation to a general molecule involving K-nuclei and N-electrons. Mathematically this problem is to extremize $\mathscr{E}$ defined by (2.8) with (2.2) on the set $\mathscr{S}_N$ defined by (2.9).

For this analysis, our basic function space is

$$X = H_0^1(B_R\,;\mathbb{R}^N) = \left\{ \Phi = (\phi_1, \ldots, \phi_N) : \phi_j \in H_0^1(B_R) \quad \text{for } 1 \leq j \leq N \right\} .$$

X will be a reflexive Banach space with the norm

$$\|\Phi\|_X^2 = \sum_{j=1}^N \|\nabla\phi_j\|^2 . \tag{8.1}$$

The functional $\mathscr{E}$ defined by (2.8) and (2.2), can be written as

$$\mathscr{E}(\Phi) = \sum_{j=1}^N \left[\int \left[\frac{1}{2} |\nabla\phi_j|^2 - V|\phi_j|^2 \right] dx \right] + I_3(\Phi) \tag{8.2}$$

where V is defined by (2.2) and $I_3 : X \to [0, \infty]$ is defined by

$$I_3(\Phi) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \iint \frac{\phi_i(x)^2 \, \phi_j(y)^2}{|x-y|} \, dx \, dy . \tag{8.3}$$

Henceforth all sums will be from 1 to N unless otherwise indicated. To show the existence of minimizers of $\mathscr{E}$ on $\mathscr{S}_N$ we shall show that $\mathscr{E}$ is weakly l.s.c. and coercive on X and $\mathscr{S}_N$ is weakly closed in X.

LEMMA 8.1 : *I_3 is weakly continuous on X.*

Proof: It suffices to show that for each i, j obeying $1 \le i \ne j \le N$

$$\mathscr{Q}(\phi_i, \phi_j) = \iint \frac{\phi_i(x)^2 \, \phi_j(y)^2}{|x-y|} \, dx \, dy \tag{8.4}$$

is weakly continuous as the sum of weakly continuous functionals is weakly continuous. Take $i = 1$, $j = 2$ and assume $\{\phi_k^{(n)} : n \ge 1\}$ are sequences in $H_0^1(B_R)$ which converge weakly to a limit ϕ_k, $k = 1, 2$. Then

$$\left| \mathscr{Q}(\phi_1^{(n)}, \phi_2^{(n)}) - \mathscr{Q}(\phi_1, \phi_2) \le \iint |x-y|^{-1} \, [\phi_1(x)^2 \, [\phi_2^{(n)}(y)^2 - \phi_2(y)^2] + \right.$$
$$+ \phi_2^{(n)}(y)^2 \, [\phi_1^{(n)}(x)^2 - \phi_1(x)^2]] \, dx \, dy .$$

Consider

$$\int \frac{|\phi_2^{(n)}(y)^2 - \phi_2(y)^2|}{|x-y|} \, dy = \int \frac{|\phi_2^{(n)}(y) - \phi_2(y)| \; |\phi_2^{(n)}(y) + \phi_2(y)|}{|x-y|} \, dy$$
$$\le \|\phi_2^{(n)} - \phi_2\| \left[\int \frac{|\phi_2^{(n)}(y) + \phi_2(y)|^2}{|x-y|^2} \right]^{1/2}$$

using Schwarz' inequality,

$$\le 2 \|\phi_2^{(n)} - \phi_2\| \; \|\nabla \phi_2^{(n)} + \nabla \phi_2\| \tag{8.5}$$

from Hardy's inequality (3.1).

Since $\phi_2^{(n)}$ converges weakly to ϕ_2 in $H_0^1(B_R)$, then $\|\nabla \phi_2^{(n)} + \nabla \phi_2\|$ is bounded, so (8.5) becomes

$$\int \frac{|\phi_2^{(n)}(y)^2 - \phi_2(y)^2|}{|x-y|} \, dy \le M_2 \|\phi_2^{(n)} - \phi_2\|$$

for some constant M_2. There is a similar inequality with $\phi_1^{(n)}$, ϕ_1 in place of

$\phi_2^{(n)}$, ϕ_2 and then

$$\left|\mathcal{Q}(\phi_1^{(n)}, \phi_2^{(n)}) - \mathcal{Q}(\phi_1, \phi_2)\right| \leq \int [\phi_1(x)^2 M_2 \|\phi_2^{(n)} - \phi_2\|]\, dx + \int \phi_2^{(n)}(y)^2 M_1 \|\phi_1^{(n)} - \phi_1\|\, dy$$

$$= M_1 \|\phi_1^{(n)} - \phi_1\| \; \|\phi_2^{(n)}\|^2 + M_2 \|\phi_2^{(n)} - \phi_2\| \; \|\phi_1\|^2 .$$

When $\phi_k^{(n)}$ converges weakly to ϕ_k in $H_0^1(B_R)$, then it converges strongly to ϕ_k in $L^2(B_R)$ and the sequences are bounded in $L^2(B_R)$ so this estimate shows that $\mathcal{Q}$, and thus I_3, is weakly continuous.

THEOREM 8.1 : *There is a $\hat{\Phi}$ in $\mathcal{S}_N$ which minimizes $\mathcal{E}$ on $\mathcal{S}_N$ and $\mathcal{E}_0 = \mathcal{E}(\hat{\Phi})$ is finite.*

Proof : Lemma 3.1 shows that $\mathcal{S}_N$ is weakly closed in X, so it suffices to show that $\mathcal{E}$ is weakly l.s.c. and coercive on $\mathcal{S}_N$. The results of section 4 and the preceding Lemma 8.1 shows that $\mathcal{E}$ is weakly l.s.c. on X.

When $\mathcal{Q}$ is defined by (8.4) we see that

$$\mathcal{Q}(\phi_i, \phi_j) \geq \frac{1}{2R} \iint \phi_i(x)^2 \phi_j(y)^2\, dx\, dy = \frac{1}{2R} .$$

Thus, just as in the proof of Lemma 4.4 and using the fact that V defined by (2.2) is in $L^q(B_R)$ for $1 \leq q < 3$, we have that $\mathcal{E}(\Phi) \geq \frac{1}{2} \|\nabla \Phi\|^2 - C$ for some constant C and when Φ is in $\mathcal{S}_N$. Thus $\mathcal{E}$ is coercive, so $\mathcal{E}$ attains its infimum on $\mathcal{S}_N$ and this infimum is finite.

To obtain the equation obeyed at the extrema of $\mathcal{E}$ on $\mathcal{S}_N$, we will show that $\mathcal{E}$ is Gateaux differentiable on X. Its derivative is the element $\mathcal{E}'(\Phi)$ of X^* obeying

$$\lim_{t \to \infty} t^{-1}[\mathcal{E}(\Phi + t\Psi) - \mathcal{E}(\Phi)] = \langle \mathcal{E}'(\Phi), \Psi \rangle$$

for all Ψ in X. Here $\langle , \rangle$ will be the standard pairing of X and X^* *via* the inner product on $L^2(B_R ; \mathbb{R}^N)$.

LEMMA 8.2 : *Assume V obeys (V1), then $\mathcal{E}$ is Gateaux differentiable at each Φ in X and*

$$\langle \mathcal{E}'(\Phi), \Psi \rangle = \int \sum_{j=1}^{N} \left[\nabla \phi_j(x) \nabla \psi_j(x) - 2V(x) \phi_j \psi_j + 2 \psi_j(x) \phi_j(x) \sum_{i \neq j} \int \frac{\phi_i(y)^2}{|x - y|} dy \right] dx \quad (8.6)$$

for each Ψ in X.

Proof : The first two terms in (8.6) arise just as in Lemma 4.5 where we use the fact that V is in $L^q(B_R)$ for $1 \leqslant q < 3$.

Consider

$$\begin{aligned}\sigma(t) &= I_3(\Phi + t\Psi) \\ &= \frac{1}{2}\sum_{i=1}^{N}\sum_{j \neq i} \mathcal{Q}(\phi_i + t\psi_i, \phi_j + t\psi_j) = \sum_{j \neq i} \sigma_{ij}(t)\end{aligned}$$

where $\mathcal{Q}$ is defined by (8.4). Now $\sigma_{ij}(t)$ is a quartic polynomial in t and one sees that

$$\sigma'_{ij}(0) = \iint [\phi_i(x)\,\psi_i(x)\,\phi_j(y)^2 + \phi_i(x)^2\,\phi_j(y)\,\psi_j(y)]\,|x-y|^{-1}\,dx\,dy\,.$$

Thus

$$\sigma'(0) = 2\int \sum_{i=1}^{N} \psi_i(x)\,\phi_i(x)\left(\sum_{j \neq i}\int \phi_j(y)^2\,|x-y|^{-1}\,dy\right)dx$$

and this leads to (8.6). □

THEOREM 8.2 : *When V is defined by* (2.2) *and $\hat{\Phi}$ minimizes $\mathcal{E}$ given by* (8.2) *on $\mathcal{S}_N$, then $\hat{\Phi} = (\hat{\phi}_1, \ldots, \hat{\phi}_N)$ obeys*

$$-\frac{1}{2}\Delta\phi_i(x) + \phi_i(x)\left[\sum_{j \neq i}\int \frac{\phi_j(y)^2}{|x-y|}\,dy - V(x)\right] = \lambda_i\,\phi_i \quad on\ B_R \tag{8.7}$$

$$\phi_i(x) = 0 \quad on\ |x| = R \tag{8.8}$$

$$and \quad \int \phi_i(x)^2\,dx = 1 \tag{8.9}$$

for $1 \leqslant i \leqslant N$ and for some real numbers $(\lambda_1, \ldots, \lambda_N)$. Moreover

$$\mathcal{E}(\hat{\Phi}) + I_3(\hat{\Phi}) = \sum_{i=1}^{N} \lambda_i\,. \tag{8.10}$$

Proof : Arguing just as in the proof of Theorem 4.2, the minimizer of $\mathcal{E}$ on $\mathcal{S}_N$ obeys

$$\left\langle \mathcal{E}'(\hat{\Phi}), \Psi \right\rangle = \sum_{i=1}^{N} \lambda_i \int \phi_i\,\psi_i\,dx$$

for all Ψ in X and some real numbers $\lambda_1, \ldots, \lambda_N$.

Use (8.6), then $\hat{\Phi}$ will be a weak solution of (8.7) and, since $\hat{\Phi}$ is in $\mathcal{S}_N$, (8.8) and (8.9) hold for each i.

Multiply each equation of the form (8.7) by ϕ_i and sum, then

$$-\sum_{i=1}^{N}\left[\frac{1}{2}\int \phi_i\,\Delta\phi_i + \int V(x)\,\phi_i^2\right] + \\ + \sum_{i\neq j}\int \phi_i(x)^2\,dx\left(\int \frac{\phi_i(y)^2}{|x-y|}\,dy\right) = \sum \lambda_i\,.$$

Therefore $\sum_{i=1}^{N}\left[\frac{1}{2}\int |\nabla\hat{\phi}_i|^2\,dx - I_1(\hat{\phi}_i)\right] + 2\,I_3(\hat{\Phi}) = \sum \lambda_i\,.$

Substituting from (8.2) we find (8.10).

This Theorem shows that the minimizer of $\mathscr{E}$ on $\mathscr{S}_N$ is actually a solution of the usual Hartree eigenproblem (2.11) for an N-electron system with the potential V.

9. MODIFIED VARIATIONAL PRINCIPLES

In this section we shall describe and analyze a variational principle whose domain is a closed convex set in X and which has the same minimizers as the general Hartree problem $(\mathscr{H}a)$ described in the previous section. Our work here parallels the development of section 5 and section 6 for the Helium atom.

Consider the problem $(\mathscr{P}\mathscr{H}a)$ of minimizing

$$\mathscr{F}_\eta(\Phi) = \mathscr{E}(\Phi) - \frac{\eta}{2}\sum_{j=1}^{N}\|\phi_j\|^2 \tag{9.1}$$

on the unit product ball

$$\mathscr{B}_N = \{\Phi \in X : \|\phi_j\| \leq 1 \text{ for } 1 \leq j \leq N\} \tag{9.2}$$

where $\mathscr{E}$ is defined by (8.2) and $\eta \geq 0$.

THEOREM 9.1 : *Assume V is given by (2.2) and $\eta \geq 0$. Then there is a $\hat{\Phi}_\eta = (\phi_{\eta 1}, \ldots, \phi_{\eta N})$ in $\mathscr{B}_N$ which minimizes $\mathscr{F}_\eta$ on $\mathscr{B}_N$. It satisfies*

$$D_{\phi_j}\mathscr{E}(\Phi) - \eta\,\phi_j = \mu_j\,\phi_j \tag{9.3}$$

for some μ in $\mathbb{R}^N$ and for $1 \leq j \leq N$. If $\|\hat{\phi}_{\eta j}\| < 1$ then $\mu_j = 0$, and if $\mu_j \neq 0$ then $\|\hat{\phi}_{\eta j}\| = 1$.

Proof: This follows from the analysis of section 8 just as was done in Theorem 5.2. □

The system of equations (9.3) says that each $\hat{\phi}_{\eta j}$ is an element of $\mathscr{B}_N$ which is a weak solution of

$$-\frac{1}{2}\Delta\phi_j + (W_j(x) - V(x))\,\phi_j = (\eta + \mu_j)\,\phi_j \tag{9.4}$$

on B_R where

$$W_j(x) = \sum_{k \neq j} \int \frac{\phi_k(y)^2}{|x-y|}\, dy . \tag{9.5}$$

LEMMA 9.1 : *Let* $\hat{\Phi}_\eta$ *minimize* $\mathcal{F}_\eta$ on $\mathcal{B}_N$, *then there is a constant* C_1 *independent of* η *such that*

$$\| \hat{\Phi}_\eta \|_X^2 \leqslant C_1 . \tag{9.6}$$

Proof : From (8.2), since $I_3(\Phi) \geqslant 0$

$$\mathcal{E}(\Phi) = \frac{1}{2} \sum_{j=1}^{N} \mathcal{H}_V(\phi_j) = \frac{1}{2} \sum_{j=1}^{N} \int [|\nabla \phi_j|^2 - 2\, V(x)\, \phi_j(x)^2]\, dx$$

where each $\mathcal{H}_V$ has the form (5.1) with V given by (2.2).

Now $V \in L^q(B_R)$ for $q < 3$ so take $q = 2$

$$\left| \int V \phi^2 \right| \leqslant \| V \|_2 \, \| \phi \|_4^2$$

and using Theorem 3.1, for any $\varepsilon > 0$, there is a $C(\varepsilon) > 0$ such that $\| \phi \|_4^2 \leqslant \varepsilon \, \| \nabla \phi \|^2 + C(\varepsilon) \, \| \phi \|^2 \leqslant \varepsilon \, \| \nabla \phi \|^2 + C(\varepsilon)$ when $\| \phi \|_2 \leqslant 1$. Thus

$$\begin{aligned} \mathcal{E}(\Phi) &\geqslant \frac{1}{2} (1 - \varepsilon \| V \|_2) \sum_{j=1}^{N} \int |\nabla \phi_j|^2 - \| V \|_2 \, C(\varepsilon) \sum_{j=1}^{N} \| \phi j_j \|^2 \\ &\geqslant \frac{1}{2} (1 - \varepsilon \| V \|_2) \| \Phi \|_X^2 - C(\varepsilon) \| V \|_2 \, N \end{aligned} \tag{9.7}$$

Now $\mathcal{F}_\eta(\hat{\Phi}_\eta) \leqslant \mathcal{E}_0 - \frac{\eta}{2} N = \inf\limits_{\Phi \in \mathcal{S}_N} \mathcal{F}_\eta(\Phi)$ so

$$\mathcal{E}(\hat{\Phi}_\eta) - \frac{\eta}{2} \left\| \hat{\Phi}_\eta \right\|^2 \leqslant \mathcal{E}_0 - \frac{\eta}{2} N .$$

Therefore

$$\mathcal{E}(\hat{\Phi}_\eta) \leqslant \mathcal{E}_0 - \frac{\eta}{2} (N - \left\| \hat{\Phi}_\eta \right\|^2) \quad \text{if} \quad \eta \geqslant 0 .$$

Using (9.7) here we see that provided ε is chosen so small that $\varepsilon \| V \|_2 < 1$, then (9.6) follows as the coefficient of η is always non-positive. □

It is worth noting that the value of C_1 depends essentially only on the potential V and the radius R of the domain.

COROLLARY 9.1 : *Assume V is given by* (2.2) *and* $(W_1, \dots, W_N)$ *are defined by* (9.5) *with* $\hat{\Phi}_\eta = (\phi_1, \dots, \phi_N)$. *Then there is a constant* C_2 *independent of* η *such that*

$$0 \leq W_j(x) \leq C_2 \quad \text{on} \quad B_R . \tag{9.8}$$

Proof: We have $W_j(x) = Q(f_j(x))$ where Q is defined by (3.4) and $f_j(x) = \sum_{k \neq j} \hat{\phi}_{\eta j}(x)^2$. Thus $\|f_j\|_1 \leq N - 1$ since $\hat{\Phi}_\eta$ is in $\mathscr{B}_N$ and

$$\frac{\partial f_j(x)}{\partial x_\ell} = \sum_{k \neq j} 2\, \hat{\phi}_{\eta j}(x) \frac{\partial \hat{\phi}_{\eta j}(x)}{\partial x_\ell}$$

so f_j is in $W_0^{1,3/2}(B_R)$ as each $\phi_{\eta j}$ is in $H_0^1(B_R)$ and using the Hölder's and Sobolev inequalities. From (9.6), there is a constant K_1 independent of η such that

$$\|f_j\|_{1,3/2} \leq K_1 \quad \text{for} \quad 1 \leq j \leq N .$$

The Sobolev embedding theorem implies that each f_j is in $L^p(B_R)$ for $1 \leq p \leq 3$ and $\|f_j\|_3 \leq K_2$ with K_2 independent of η.

Young's inequality for convolutions now yields that

$$\|W_j\|_\infty \leq \| |x|^{-1} \|_{p'} \|f_j\|_p .$$

This will be finite as when $p > 3/2$, then $3/2 < p' < 3$ and both these factors will be finite. This implies (9.8) with C_2 independent of η. □

THEOREM 9.2 : *Assume V is given by* (2.2), $\lambda_1(V)$ *is defined by* (5.2), C_2 *is a constant such that* (9.8) *holds and let* $\eta_c = C_2 + 2\lambda_1(V)$. *If* $\eta > \eta_c$ *and* $\hat{\Phi}_\eta$ *minimizes* $\mathscr{F}_\eta$ *on* $\mathscr{B}_N$, *then* $\hat{\Phi}_\eta$ *minimizes* $\mathscr{E}$ *on* $\mathscr{S}_N$.

Proof: Suppose $\hat{\Phi}_\eta$ minimizes $\mathscr{F}_\eta$ on $\mathscr{B}_N$ and choose j in $\{1, 2, \dots, N\}$. Fix $\hat{\phi}_{\eta k}$ for $k \neq j$, then $\hat{\phi}_{\eta j}$ must minimize $\mathscr{F}_\eta$ as a function of ϕ_j alone on $\mathscr{B}$ defined by (5.4). That is $\hat{\phi}_{\eta j}$ minimizes

$$\mathscr{H}_j(\phi) - \frac{\eta}{2} \|\phi\|^2 = \int \left[\frac{1}{2} |\nabla \phi|^2 + \left(\frac{1}{2}(W_j - \eta) - V \right) \phi^2 \right] dx \tag{9.9}$$

on $\mathscr{B}$. Here W_j is given by (9.5) with $\phi_{\eta k}$ in place of ϕ_k. This is a quadratic functional in ϕ. Define

$$\lambda_{1j}(V) = \inf_{\|\phi\| \leq 1} \mathscr{H}_j(\phi) \leq \lambda_1(V) + C_2/2 \tag{9.10}$$

where $\lambda_1(V)$ is given by (5.2) and W_j obeys (9.8).

When $\lambda_{1j}(V) - \frac{\eta}{2} < 0$, the infimum of (9.9) occurs at a function $\hat{\phi}_{\eta j}$ obeying $\|\hat{\phi}_{\eta j}\| = 1$. In particular if $\eta > 2\lambda_1(V) + C_2$, then $\|\hat{\phi}_{\eta j}\| = 1$ for $1 \leq j \leq N$ from (9.10). The theorem now follows as this $\hat{\Phi}_\eta$ is in $\mathcal{S}_N$. □

To derive convergent algorithms for $(\mathcal{P}\mathcal{H}a)$ we would like to express $\mathcal{F}_\eta$ defined by (9.1) as the difference of two convex functionals. This leads to the question of the convexity of I_3. With some simple algebra, one sees that

$$2 I_3(\Phi) = \iint \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy - \sum_{i=1}^{N} \iint \frac{\phi_i(x)^2\,\phi_i(y)^2}{|x-y|}\,dx\,dy \quad (9.11)$$

where

$$\rho(x) = \sum_{i=1}^{N} |\phi_i(x)|^2 . \quad (9.12)$$

Each term of the sum in (9.11) has the form $I_2(\phi_i)$ with I_2 defined by (4.2), and Lemma 4.3 says that each of these is convex. Define $I_4 : X \to \mathbb{R}$ by

$$I_4(\Phi) = \frac{1}{2} \iint \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy \quad (9.13)$$

where ρ and Φ are related by (9.12).

LEMMA 9.2 : *The functional I_4 defined by* (9.12)-(9.13) *is non-negative, bounded, convex and weakly continuous on X.*

Proof : The proofs of non-negativity, boundedness and weak continuity are straight-forward modifications of Lemma 4.3.

When Φ, Ψ are in X, let $g(t) = I_4(\Phi + t\Psi)$. Then g is a quartic polynomial in t and one finds that

$$g''(t) = 2 \iint |x-y|^{-1}[|\Phi(x)|^2\,|\Psi(y)|^2 + \\ + 2(\Phi(x).\Psi(x))(\Phi(y).\Psi(y))]\,dx\,dy$$

using the usual Euclidean norms and inner products on $\mathbb{R}^N$. Each term on this right hand side is non-negative as in the proof of Lemma 4.3 so I_4 is convex by corollary 42.8 in [23]. □

This analysis shows that I_3 is a non-negative, bounded and weakly continuous functional on X which can be written as the difference of two convex functionals

$$I_3(\Phi) = I_4(\Phi) - \frac{1}{2}\sum_{i=1}^{N} I_2(\phi_i) . \quad (9.14)$$

10. SEPARATELY CONVEX FORMULATION

In the last section, we described a variational principle $(\mathscr{P}\mathscr{H}a)$ for the N-electron Hartree problem based on minimizing $\mathscr{F}_\eta$ on the product ball $\mathscr{B}_N$ instead of on the sphere $\mathscr{S}_N$ of the usual Hartree formulation. Moreover it was shown that $\mathscr{F}_\eta$ could be written as a difference of two convex functionals. Thus the general techniques of [3] could be applied to this problem. This would involve solving for Φ, ρ and certain dual vector-valued functions at each step.

There are a number of reasons why it is advantageous to find minima by only doing descent in one component ϕ_j at a time. These include the fact that each such computation is smaller and more manageable as they typically involve solving one elliptic problem at each step instead of a system of N elliptic problems. Here we shall describe a variational formulation of the Hartree problem which involves minimizing a functional on a convex set with the functional convex in each variable separately.

Define $\mathscr{L} : X \times Y \times (0, \infty) \to \mathbb{R}$ by

$$\mathscr{L}(\Phi, \Psi ; \eta) = \\ = \sum_{j=1}^{N} \int \left[\frac{1}{2} |\nabla \phi_j|^2 + W_j \phi_j^2 - \phi_j \psi_j + \frac{1}{2} \frac{\psi_j^2}{2V + \eta} \right] dx \quad (10.1)$$

where $Y = L^{6/5}(B_R ; \mathbb{R}^N)$ and $W_j(x)$ is defined by (9.5) and is independent of ϕ_j.

The problem $(\mathscr{L}\mathscr{H}a)$ is to minimize $\mathscr{L}(\,.\,,\,.\,;\eta)$ on $\mathscr{B}_N \times Y$ and to evaluate

$$\alpha(\eta) = \inf_{\Phi \in \mathscr{B}_N} \inf_{\Psi \in Y} \mathscr{L}(\Phi, \Psi ; \eta) . \quad (10.2)$$

THEOREM 10.1 : *Assume V obeys* (V1) *and* (V2), $\eta > 0$ *and $\mathscr{L}$ is defined by* (10.1). *As a function of ϕ_ℓ, with ϕ_j, $j \neq \ell$, Ψ, η fixed, $\mathscr{L}$ is coercive, strictly convex and weakly l.s.c. on $\mathscr{B}$. For each Φ in $\mathscr{B}_N$, η, ψ_j, $j \neq \ell$ fixed then $\mathscr{L}$ is convex and l.s.c. for ψ_ℓ in $L^{6/5}(B_R)$. Moreover*

$$\mathscr{F}_\eta(\Phi) = \inf_{\Psi \in Y} \mathscr{L}(\Phi, \Psi ; \eta) . \quad (10.3)$$

Proof : This result follows just as the proof of Lemma 6.2. $\mathscr{L}$ is minimized in ψ_ℓ, keeping other variables fixed, when

$$\psi_\ell = (2V + \eta)\, \phi_\ell \quad (10.4)$$

upon using the extremality conditions for (10.1), $1 \leq \ell \leq N$. Thus

$$\inf_{\Psi \in Y} \mathscr{L}(\Phi, \Psi ; \eta) = \sum_{j=1}^{N} \int \left[\frac{1}{2} |\nabla \phi_j|^2 + W_j \phi_j^2 - (V + \eta/2) \phi_j^2 \right] dx$$

(8.3) and (8.5) leads to

$$2 I_3(\Phi) = \sum \phi_j^2 W_j \tag{10.5}$$

so (10.3) follows from the definition of $\mathscr{F}_\eta$ and $\mathscr{E}$. □

COROLLARY 10.1 : *$\hat{\Phi}_\eta$ minimizes $\mathscr{F}_\eta$ on $\mathscr{B}_N$ iff there is a $\hat{\Psi}_\eta$ in $L^{6/5}(B_R ; \mathbb{R}^N) = Y$ such that $(\hat{\Phi}_\eta, \hat{\Psi}_\eta)$ minimizes $\mathscr{L}(\,.\,,\,.\,;\eta)$ on $\mathscr{B}_N \times Y$. Then*

(i) $\hat{\Psi}_{\eta j} = (2V + \eta)\hat{\Psi}_\ell$ *for* $1 \leq \ell \leq N$, *and*
(ii) $\alpha(\eta) = \inf_{\Phi \in \mathscr{B}_N} \mathscr{F}_\eta(\Phi)$.

Proof : (ii) follows by taking the infimum of (10.3) over $\mathscr{B}_N$. If $\hat{\Phi}_\eta$ minimizes $\mathscr{F}_\eta$ on $\mathscr{B}_N$; $\hat{\Psi}_\eta$ be given by (i), then $\hat{\Psi}_\eta$ is in Y and it obeys the extremality condition for $\mathscr{L}(\hat{\Phi}_\eta, \,.\,;\eta)$ on Y. Since $\mathscr{L}$ is convex in Ψ, any extremum is a minimizer so $(\hat{\Phi}_\eta, \hat{\Psi}_\eta)$ minimizes $\mathscr{L}(\,.\,,\,.\,;\eta)$ on $\mathscr{B}_N \times Y$.

It is worth noting that $(\mathscr{H}a)$ and $(\mathscr{P}\mathscr{H}a)$ may have critical points which are not minimizers of $\mathscr{E}$ on $\mathscr{S}$ and $\mathscr{F}_\eta$ on $\mathscr{B}_N$ respectively. These critical points will be solutions of the Hartree equations (8.7)-(8.9) which are not the ground-state of the system. Further analysis of (10.1) shows that, provided η is large enough, there will be corresponding critical points of (10.1) which are not global minimizers and whose Φ components are solutions of the Hartree equations.

11. DESCENT ALGORITHMS FOR THE HARTREE EIGEN-PROBLEM

In the Preceding section, we showed that the variational principle $(\mathscr{L}\mathscr{H}a)$ of minimizing $\mathscr{L}(\,.\,,\,.\,;\eta)$ on $\mathscr{B}_N \times Y$ is equivalent to the usual Hartree problem for an N-electron atom or molecule. This principle has the advantage that it can be treated as a sequence of well-posed, strictly convex problems each of which has a unique minimizer.

It leads to the following natural algorithm.

ALGORITHM 11.1 : *Given $\varepsilon > 0$, $\eta > 0$ and $\Phi^{(0)}$ in $\mathscr{S}_N$. For $k \geq 0$*

1. *Define*

$$\Psi^{(k)}(x) = (2V + \eta)\,\Phi^{(k)}(x)\,. \tag{11.1}$$

2. *Evaluate*

$$W_j^{(k)} = \sum_{\ell \neq j} \int \frac{\phi_\ell^{(k)}(y)^2}{|x-y|}\, dy \tag{11.2}$$

for $1 \leqslant j \leqslant N$.

3. *Evaluate*

$$d_j^{(k)}(x) = -\Delta \phi_j^{(k)} + (2\, W_j^{(k)}(x) - \Psi_j^{(k)}(x))\, \phi_j^{(k)} \tag{11.3}$$

for $1 \leqslant j \leqslant N$.

4. *Compute*

$$\rho_k = \| d^{(k)} - \langle d^{(k)}, \Phi^{(k)} \rangle\, \Phi^{(k)} \| \,.$$

5. *If* $\rho_k \leqslant \varepsilon$ *stop, else continue.*

6. *For* $1 \leqslant j \leqslant N$, *find* $\varphi_j^{(k+1)}$ *as the minimizer of*

$$\mathscr{A}_j^{(k)}(\varphi) = \mathscr{L}(\phi_1^{(k+1)}, \ldots, \phi_{j-1}^{(k+1)}, \varphi, \phi_{j+1}^{(k)}, \ldots, \phi_N^{(k)}, \Psi^{(k)}; \eta) \tag{11.4}$$

with φ *in* $\mathscr{B}$ *defined by* (5.4).

7. *Put* $\Phi^{(k+1)} = (\varphi_1^{(k+1)}, \ldots, \varphi_N^{(k+1)})$, $k+1$ *in place of* k *and go to* 1.

Here step 1 uses the explicit expression (10.4) for minimizing $\mathscr{L}(\Phi^{(k)}, \cdot\,; \eta)$ as a function of Ψ.

In steps 2 and 3, $W_j^{(k)}$ is the appropriate function corresponding to (9.5) and then $d^{(k)}$ is the derivative of $\mathscr{L}(\cdot\,, \Psi^{(k)}; \eta)$ with respect to Φ ; evaluated at $\Phi^{(k)}$. ρ_k measures whether $\Phi^{(k)}$ is an approximate eigensolution of the problem. If so, we stop.

In step 6, we compute the next $\Phi^{(k+1)}$ by minimizing $\mathscr{L}$ with respect to $\varphi_1, \varphi_2, \ldots, \varphi_N$ in each function φ_j separately. Thus $\varphi_j^{(k+1)}$ will be a solution of the system of equations

$$-\Delta\phi + [2\, \tilde{W}_j^{(k)}(x) - \psi_j^{(k)}(x)]\, \phi = \mu \phi \quad \text{in} \quad B_R \tag{11.5}$$

$$\phi = 0 \quad \text{on} \quad |x| = R \tag{11.6}$$

and

$$\int \phi^2\, dx \leqslant 1 \,. \tag{11.7}$$

Here

$$\tilde{W}_j^{(k)}(x) = \int |x-y|^{-1} \left[\sum_{\ell=1}^{j-1} |\phi_\ell^{(k+1)}(y)|^2 + \sum_{\ell=j+1}^{N} |\phi_\ell^{(k)}(y)|^2 \right] dy \,.$$

For $\eta \geqslant \eta_c$ and when we are close enough to a solution it is expected that equality will hold in (11.7).

Just as in section 7, it can be shown that the sequence $\{(\Phi^{(k)}, \Psi^{(k)}) : k \geqslant 0\}$ generated by algorithm 11.1 from an arbitrary initial choice $\Phi^{(0)}$ will be a descent sequence for $\mathscr{L}(\,.\,,\,.\,;\eta)$ and

$$\mathscr{L}(\Phi^{(k+1)}, \Psi^{(k+1)}; \eta) = \mathscr{L}(\Phi^{(k)}, \Psi^{(k)}; \eta)$$

if and only if $\Phi^{(k)}$ is in $\mathscr{B}_N$ and obeys (8.7)-(8.8).

We may summarize these results as follows.

THEOREM 11.1 : *Assume* V *is defined by* (2.2), $\varepsilon = 0$, $\eta > 0$ *and* $\Phi^{(0)}$ *is in* $\mathscr{B}_N$. *If* $\Gamma = \{\Phi^{(k)} : k \geqslant 0\}$ *is the sequence generated by algorithm* 11.1 *then either :*

(i) Γ *is finite and the last* $\Phi^{(k)}$ *is a solution of the Hartree eigenproblem* (8.7)-(8.8), *or*

(ii) Γ *is an infinite bounded sequence in* $\mathscr{B}_N$ *which is a strict descent sequence for* $\mathscr{F}_\eta$ *and* Γ *has at least one weak limit point in* $\mathscr{B}_N$. *If* $\hat{\Phi}$ *is a strong limit point of* Γ, *then* $\hat{\Phi}$ *is a solution of* (8.7)-(8.8).

Proof : This proof follows in a similar manner to that of Theorem 7.1. Unfortunately unlike the proof of Theorem 7.1, we have not been able to show that each weak limit point of Γ is a strong limit point of Γ in this case. For this problem $\mathscr{L}(\,.\,,\Psi\,;\eta)$ is non-convex on $\mathscr{B}$ so the methods used in section 7 do not carry over to provide an estimate analogous to (7.11). □

12. A CONVERGENT DESCENT ALGORITHM

In Auchmuty [3], some general algorithm for minimizing the difference of two convex functional and certain convergent results were proven. The problem $(\mathscr{P}\mathscr{H}a)$ described in section 9 has this form, so we shall describe the corresponding algorithm based on [3]. As will be seen, this algorithm is closely related to that of the previous section.

We shall now use notation corresponding to that of [3]. Take $X = H_0^1(B_R\,;\mathbb{R}^N)$, $Y = L^4(B_R\,;\mathbb{R}^N)$ and $\Lambda : X \to Y$ be the standard embedding. Then Λ is a linear, compact, 1-1 map. Compactness follows from the Kondrachov-Rellich theorem, so assumption (A5) of [3] holds.

Define $f_1 : \to [0, \infty]$ by

$$2 f_1(\Phi) = \int \sum |\nabla \phi_j|^2\, dx + \iint \frac{\rho(x)\,\rho(y)}{|x-y|}\, dx\, dy + \chi_1(\Phi) \quad (12.1)$$

where ρ is defined by (9.12) and

$$\chi_1(\Phi) = \begin{cases} 0 & \text{if} \quad \Phi \in \mathscr{B}_N \\ \infty & \text{otherwise} . \end{cases} \tag{12.2}$$

Define $f_2 : Y \times (0, \infty) \to [0, \infty)$ by

$$2 f_2(\Phi, \eta) = \int (2V + \eta) |\Phi|^2 \, dx + \sum_{j=1}^{N} I_2(\phi_j) \tag{12.3}$$

where V is defined by (2.2) and I_2 by (4.2).

Consider $F : X \to \bar{\mathbb{R}}$ defined by

$$F(\Phi) = f_1(\Phi) - f_2(\Phi ; \eta) . \tag{12.4}$$

Here the embedding Λ is understood in the expression of f_2. This has the basic form of equation of [3] and from (8.2), (9.1) and (9.14),

$$F(\Phi) = \begin{cases} \mathscr{F}_\eta(\Phi) & \text{if} \quad \Phi \in \mathscr{B}_N \\ \infty & \text{otherwise} \end{cases} \tag{12.5}$$

so $(\mathscr{P}\mathscr{H}a)$ is the problem of minimizing this F on X.

It is straightforward to verify that f_1 obeys (A1) and (A2) of section 2 in [3] and that (2.3) there holds with $\gamma_1 = 2$, $C_1 = 1/2$, $d_1 = 0$.

$f_2(. ; \eta)$ obeys (A1), is convex, continuous and bounded on Y and there are constants C_2, d_2 such that

$$0 \leqslant f_2(\Phi ; \eta) \leqslant C_2 \| \Phi \|_4^2 + d_2 \tag{12.6}$$

for all Φ in Y. Thus assumptions (A3′) and (A5) of [3] hold.

Since this problem satisfies the assumptions of the problems treated in [3], we can look at the corresponding algorithm. Algorithm $(\mathscr{A}1)$ of section 4 of [3], when applied to this N-electron Hartree problem can be written as follows.

ALGORITHM 12.1 : *Given* $\varepsilon \geqslant 0$, $\eta > 0$, $\Phi^{(0)}$ *in* $\mathscr{S}_N$. *For* $k \geqslant 0$ *and* $1 \leqslant j \leqslant N$:

1. *Define*

$$\Psi_j^{(k)}(x) = \left[2V(x) + \eta + \int \frac{|\phi_j^{(k)}(y)|^2}{|x - y|} \, dy \right] \phi_j^{(k)}(x) . \tag{12.7}$$

2. *Find* $\Phi^{(k+1)}$ *in* $\mathscr{B}_N$ *obeying*

$$\Psi^{(k)} \in \partial f_1(\Phi^{(k+1)}) . \tag{12.8}$$

3. *Evaluate*

$$d_j^{(k+1)}(x) = -\Delta\Phi_j^{(k-1)} + \left[2\int \frac{\rho^{(k+1)}(y)}{|x-y|}\,dy - \Psi_j^{(k)}(x)\right]\Phi_j^{(k+1)}.$$

4. *Evaluate*

$$\delta_k = \left\| d^{(k+1)} - \langle d^{(k+1)}, \Phi^{(k+1)}\rangle\, \Phi^{(k+1)} \right\|.$$

5. *If* $\delta_k \leqslant \varepsilon$ *stop, else put* $k = k+1$ *and go to 1.*

This description of the algorithm differs from that of [3] in that we have avoided the use of conjugate convex functionals and have given an explicit form for the Lagrangian L. Instead we have used the duality property that

$$v \in \partial f(u) \quad \text{iff} \quad u \in \partial f^*(v)$$

where $f : X \to (-\infty, \infty]$ is convex and l.s.c. (Theorem 51.A in [23]). Thus (12.6) is equivalent to step 3 in ($\mathscr{A}1$) and (12.7) is step 2 in ($\mathscr{A}1$).

If $\Phi^{(k+1)}$ is a solution of (12.8), then it minimizes

$$f_{1k}(\Phi) = f_1(\Phi) - \langle \Phi, \Psi^{(k)}\rangle \tag{12.9}$$

on X. That is $\Phi^{(k+1)}$ is in $\mathscr{B}_N$ and it satisfies

$$\begin{aligned} -\Delta\Phi_j(x) + [2\,Q(\Phi)(x) - \Phi_j^{(k)}(x)]\,\Phi_j(x) &= \mu_j\,\Phi_j(x) \quad \text{in } B_R \\ \Phi_j(x) &= 0 \quad \text{on } \partial B_R \end{aligned}$$

where

$$Q(\Phi)(x) = \int \frac{\rho(x)}{|x-y|}\,dy \quad \text{and} \quad \rho(y) = \sum_{j=1}^{N} \Phi_j(y)^2. \tag{12.11}$$

This is a non-linear integro-differential coupled eigenvalue system for $(\Phi_1, \ldots, \Phi_N)$. Since f_{1k} is strictly convex and coercive, there is a unique minimizer of this system from standard results.

Step 3 and 4 of algorithm 12.1 check to see if $\Phi^{(k+1)}$ is an approximate eigenfunction of the system. If so, stop, otherwise continue. Theorem 4.1 of [3] guarantees that the sequence $\{\Phi^{(k)} : k \geqslant 0\}$ generated by algorithm 12.1 will be a descent sequence for the associated Lagrangian, and hence for F, and $F(\Phi^{(k+1)}) = F(\Phi^{(k)})$ if and only if $\Phi^{(k)}$ is a solution of (8.7)-(8.8).

THEOREM 12.1 : *Assume* V *is defined by* (2.2), $\Phi^{(0)}$ *is in* $\mathscr{B}_N$, $\varepsilon = 0$ *and* $\eta > 0$. *Let* $\Gamma = \{\Phi^{(k)}; k \geqslant 0\}$ *be the sequence generated by algorithm* 12.1. *Then either*

(i) Γ *is finite and the last element* $\Phi^{(k)}$ *is a solution of the Hartree eigenproblem* (8.7)-(8.8), *or*

(ii) *Γ is an infinite, bounded sequence in $\mathscr{B}_N$ which is a strict descent sequence for F and which has at least one weak limit point in $\mathscr{B}_N$. Each such limit point is a solution of the eigenproblem* (8.7)-(8.8).

Proof This proof follows in the same manner as Theorem 7.1 except now all the functions are vector-valued, Φ, Ψ replace (u, w) and f_1, f_2 replace h_1, h_2. In particular the analog of (7.11) holds with $r = 4/3$ in this case. □

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