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Analytic structure of solutions to multiconfiguration equations

Søren Fournais[1,6], **Maria Hoffmann-Ostenhof**[2], **Thomas Hoffmann-Ostenhof**[3,4] **and Thomas Østergaard Sørensen**[5,7]

[1] Department of Mathematical Sciences, University of Aarhus, Ny Munkegade, Building 1530, DK-8000 Århus C, Denmark
[2] Fakultät für Mathematik, Universität Wien, Nordbergstraße 15, A-1090 Vienna, Austria
[3] Institut für Theoretische Chemie, Währingerstrasse 17, Universität Wien, A-1090 Vienna, Austria
[4] The Erwin Schrödinger International Institute for Mathematical Physics, Boltzmanngasse 9, A-1090 Vienna, Austria
[5] Department of Mathematics, Imperial College London, Huxley Building, 180 Queen's Gate, London SW7 2AZ, UK

E-mail: fournais@imf.au.dk, Maria.Hoffmann-Ostenhof@univie.ac.at, thoffman@esi.ac.at and t.sorensen@imperial.ac.uk

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Abstract

We study the regularity at the positions of the (fixed) nuclei of solutions to (non-relativistic) multiconfiguration equations (including Hartree–Fock) of Coulomb systems. We prove the following: let $\{\varphi_1, \ldots, \varphi_M\}$ be any solution to the rank-M multiconfiguration equations for a molecule with L fixed nuclei at $R_1, \ldots, R_L \in \mathbb{R}^3$. Then, for any $j \in \{1, \ldots, M\}$, $k \in \{1, \ldots, L\}$, there exists a neighborhood $U_{j,k} \subseteq \mathbb{R}^3$ of R_k, and functions $\varphi^{(1)}_{j,k}$, $\varphi^{(2)}_{j,k}$, real analytic in $U_{j,k}$, such that

$$\varphi_j(\mathbf{x}) = \varphi^{(1)}_{j,k}(\mathbf{x}) + |\mathbf{x} - R_k|\varphi^{(2)}_{j,k}(\mathbf{x}), \qquad \mathbf{x} \in U_{j,k}.$$

A similar result holds for the corresponding electron density. The proof uses the Kustaanheimo–Stiefel transformation, as applied in [9] to the study of the eigenfunctions of the Schrödinger operator of atoms and molecules near two-particle coalescence points.

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[6] On leave from: CNRS and Laboratoire de Mathématiques d'Orsay, Univ Paris-Sud, F-91405 Orsay CEDEX, France.
[7] On leave from: Department of Mathematical Sciences, Aalborg University, Fredrik Bajers Vej 7G, DK-9220 Aalborg East, Denmark.

1. Introduction and results

We consider the Hamiltonian of a molecule with N non-relativistic electrons and L (static) nuclei of (positive) charges $Z_1, \dots, Z_L$, fixed at $R_1, \dots, R_L \in \mathbb{R}^3$, given by

$$H = H(N, Z) = \sum_{j=1}^{N} \left\{ -\Delta_j + V(\mathbf{x}_j) \right\} + \sum_{1 \leqslant i < j \leqslant N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}, \tag{1}$$

$$V(\mathbf{x}) = -\sum_{k=1}^{L} \frac{Z_k}{|\mathbf{x} - R_k|}. \tag{2}$$

Here, $\mathbf{x}_j \in \mathbb{R}^3$ is the coordinate of the jth electron and Δ_j is the Laplacian with respect to $\mathbf{x}_j$. The operator H acts on a dense subspace of the N-particle Hilbert space $\mathcal{H}_F = \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3; \mathbb{C}^q)$ of antisymmetric functions, where q is the number of spin states. More precisely, its operator domain is $\mathcal{D}(H) = \bigwedge_{i=1}^{N} W^{2,2}(\mathbb{R}^3; \mathbb{C}^q)$ and its quadratic form domain is $\mathcal{Q}(H) = \bigwedge_{i=1}^{N} W^{1,2}(\mathbb{R}^3; \mathbb{C}^q)$ [16, 27]. Since the spin is irrelevant for the discussion in this paper, we let $q = 1$ from now on to simplify notation. In the case most relevant for physics, namely electrons in a molecule, q takes the value 2.

Let $\mathfrak{q}$ be the quadratic form defined by H, that is, for $\Psi \in \mathcal{D}(H)$, $\mathfrak{q}(\Psi, \Psi) = \langle \Psi, H\Psi \rangle$. Then, for $\Psi \in \mathcal{Q}(H)$, (with $\mathbf{X} = (\mathbf{x}_1, \dots, \mathbf{x}_N) \in \mathbb{R}^{3N}$),

$$\mathfrak{q}(\Psi, \Psi) = \sum_{j=1}^{N} \int_{\mathbb{R}^{3N}} |\nabla_j \Psi(\mathbf{X})|^2 \, \mathrm{d}\mathbf{X} + \int_{\mathbb{R}^{3N}} \left\{ \sum_{j=1}^{N} V(\mathbf{x}_j) + \sum_{1 \leqslant i < j \leqslant N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} \right\} |\Psi(\mathbf{X})|^2 \, \mathrm{d}\mathbf{X}. \tag{3}$$

Here, ∇_j is the gradient with respect to $\mathbf{x}_j$ and $\langle \cdot, \cdot \rangle$ is the scalar product in $\mathcal{H}_F \subset L^2(\mathbb{R}^{3N})$. The quadratic form $\mathfrak{q}$ is bounded from below. The *quantum ground-state energy* is the infimum of this quadratic form:

$$\begin{aligned} E^{\mathrm{QM}}(N, Z) &:= \inf \sigma_{\mathcal{H}_F}(H) \\ &= \inf\{\mathfrak{q}(\Psi, \Psi) | \Psi \in \mathcal{Q}(H), \langle \Psi, \Psi \rangle = 1\}. \end{aligned} \tag{4}$$

The Euler–Lagrange equation for the minimization problem (4) is nothing but the (stationary) Schrödinger equation,

$$H\Psi = E\psi, \qquad \Psi \in \mathcal{D}(H), \tag{5}$$

with $E \equiv E^{\mathrm{QM}}(N, Z)$. A *ground state* of the atom is a solution to (5) for $E = E^{\mathrm{QM}}(N, Z)$; *excited states* of the atom are solutions to (5) with $E > E^{\mathrm{QM}}(N, Z)$. Zhislin [29] proved the existence of both ground states and (infinitely many) excited states, when the total charge $Z = \sum_{k=1}^{L} Z_k$ satisfies $N < Z + 1$ (see also [11]). In particular, in this case the infimum in (4) is attained, i.e., *minimizers* exist. On the other hand, Lieb [21, 22] proved that *if* minimizers exist, then $N < 2Z + L$.

Since, in practice (i.e., numerically), solving (4), or (5), is unfeasible for even relatively small N, various approximations to the problem (4) have been developed; for a comprehensive discussion of approximations in quantum chemistry and an extensive literature list, we refer to [18, 19]. We will not discuss the problems (4)–(5) further in this paper, but rather investigate (in the spirit of [9]) the solutions to the Euler–Lagrange equations for one of the most used approximations: the multiconfiguration self-consistent field method (MC-SCF) (including Hartree–Fock theory). We now discuss this in more detail.

In the perhaps most well-known approximation, the *Hartree–Fock approximation*, instead of minimizing the functional $\mathfrak{q}$ in the entire (linear) N-particle space $\mathcal{H}_F$ (or rather, $\mathcal{Q}(H)$), one restricts to wavefunctions Ψ which are pure wedge products, also called *Slater determinants*:

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det(u_i(\mathbf{x}_j))_{i,j=1}^N \equiv |u_1 \ldots u_N\rangle(\mathbf{x}_1, \ldots, \mathbf{x}_N), \tag{6}$$

with $\{u_i\}_{i=1}^N \subset W^{1,2}(\mathbb{R}^3)$, orthonormal in $L^2(\mathbb{R}^3)$ (called *orbitals*). Note that this way, $\Psi \in \mathcal{H}_F$ and $\|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1$.

The *Hartree–Fock ground-state energy* is the infimum of the quadratic form $\mathfrak{q}$ defined by H over such Slater determinants,

$$E^{\mathrm{HF}}(N, Z) := \inf\{\mathfrak{q}(\Psi, \Psi) | \Psi \in \mathcal{S}_N\}, \tag{7}$$

$$\mathcal{S}_N = \{\Psi = |\, u_1 \ldots u_N\rangle \mid u_i \in W^{1,2}(\mathbb{R}^3), (u_i, u_j) = \delta_{ij}\}, \tag{8}$$

where $(\cdot, \cdot)$ is the scalar product in $L^2(\mathbb{R}^3)$. Clearly, $E^{\mathrm{HF}}(N, Z) \geqslant E^{\mathrm{QM}}(N, Z)$. In fact, strict inequality holds [17]. Inserting Ψ of the form in (6) into (3) yields

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(u_1, \ldots, u_N) &:= \mathfrak{q}(\Psi, \Psi) \\ &= \sum_{j=1}^N \int_{\mathbb{R}^3} \left\{|\nabla u_j(\mathbf{x})|^2 + V(\mathbf{x})|u_j(\mathbf{x})|^2\right\} \mathrm{d}\mathbf{x} \\ &\quad + \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y} - \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{|\gamma(\mathbf{x}, \mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y},\end{aligned} \tag{9}$$

where ρ is the *density* and γ is the *density matrix* of Ψ, given by

$$\gamma(\mathbf{x}, \mathbf{y}) = \sum_{i=1}^N \overline{u_i(\mathbf{y})} u_i(\mathbf{x}), \qquad \rho(\mathbf{x}) = \gamma(\mathbf{x}, \mathbf{x}) = \sum_{i=1}^N |u_i(\mathbf{x})|^2. \tag{10}$$

With $\mathcal{E}^{\mathrm{HF}}$ defined this way, the minimization problem (7)–(8) can be formulated as

$$E^{\mathrm{HF}}(N, Z) = \inf\{\mathcal{E}^{\mathrm{HF}}(u_1, \ldots, u_N) | (u_1, \ldots, u_N) \in \mathcal{M}_N\}, \tag{11}$$

$$\mathcal{M}_N = \{(u_1, \ldots, u_N) \in [W^{1,2}(\mathbb{R}^3)]^N \mid (u_i, u_j) = \delta_{ij}\}. \tag{12}$$

Both the energy functional $\mathcal{E}^{\mathrm{HF}}$ and the space $\mathcal{M}_N$ are nonlinear, but the orbitals $\{u_i\}_{i=1}^N$ depend only on $\mathbf{x} \in \mathbb{R}^3$, whereas Ψ in (4) depends on $\mathbf{X} \in \mathbb{R}^{3N}$. It is this reduction in the dimension of the variables which makes the problem (11)–(12) more tractable in practice (i.e., numerically) than (4).

The existence of minimizers (again, when $Z > N - 1$) for the problem (11)–(12) (these are not unique since $\mathcal{E}^{\mathrm{HF}}$ is not convex; see also below) was first proved by Lieb and Simon [23]. The Euler–Lagrange equations of the problem (11)–(12) are the *Hartree–Fock equations* (HF equations),

$$\begin{aligned}(-\Delta + V)\varphi_i(\mathbf{x}) + \left(\sum_{j=1}^N \int_{\mathbb{R}^3} \frac{|\varphi_j(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{y}\right)\varphi_i(\mathbf{x}) - \sum_{j=1}^N \left(\int_{\mathbb{R}^3} \frac{\varphi_j(\mathbf{y})\varphi_i(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{y}\right)\varphi_j(\mathbf{x}) \\ = \varepsilon_i\varphi_i(\mathbf{x}), \qquad 1 \leqslant i \leqslant N.\end{aligned} \tag{13}$$

Here, the ε_i's are the Lagrange multipliers of the orthonormality constraints in (12). Note that the naive Euler–Lagrange equations are more complicated than (13), but since both the functional $\mathcal{E}^{\mathrm{HF}}$ in (9) and the orthogonality constraints in (12) are invariant under unitary

transformations (i.e., if $(u_1, \dots, u_N) \in \mathcal{M}_N$ and $(\tilde{u}_1, \dots, \tilde{u}_N) = U(u_1, \dots, u_N)$ for U an $N \times N$ unitary matrix, then $\mathcal{E}^{\mathrm{HF}}(\tilde{u}_1, \dots, \tilde{u}_N) = \mathcal{E}^{\mathrm{HF}}(u_1, \dots, u_N)$ and $(\tilde{u}_1, \dots, \tilde{u}_N) \in \mathcal{M}_N$), the *matrix* of Lagrange multipliers due to (12) may be diagonalized without loss of generality, which turns the Euler–Lagrange equations into (13).

In [23] it was also proved that if $(\varphi_1, \dots, \varphi_N) \in \mathcal{M}_N$ is a minimizer of the problem (11)–(12), then $\{\varphi_1, \dots, \varphi_N\}$ satisfies (13); they are called *ground-state solutions* of (13). Lions [24] proved (also for $Z > N - 1$) the existence of *saddle points*, namely, an infinite sequence $\{\varphi_n\}_{n\in\mathbb{N}} = \left\{\{\varphi_1^n, \dots, \varphi_N^n\}\right\}_{n\in\mathbb{N}}$ of solutions of (13). (We refer to [20] for a discussion of the relationship between these saddle points and the earlier mentioned excited states.) Note that (13) can be re-formulated as

$$h_\varphi \varphi_i = \varepsilon_i \varphi_i, \qquad 1 \leqslant i \leqslant N, \tag{14}$$

with h_φ being the *Hartree–Fock operator associated with* $\varphi = \{\varphi_1, \dots, \varphi_N\}$, given by

$$h_\varphi u = (-\Delta + V)u + R_\varphi u - K_\varphi u, \tag{15}$$

where V is given by (2), $R_\varphi u$ is the *direct interaction*, given by the multiplication operator defined by

$$R_\varphi(\mathbf{x}) := \sum_{j=1}^{N} \int_{\mathbb{R}^3} \frac{|\varphi_j(\mathbf{y})|^2}{|\mathbf{x} - \mathbf{y}|}\, \mathrm{d}\mathbf{y}, \tag{16}$$

and $K_\varphi u$ is the *exchange term*, given by the integral operator

$$(K_\varphi u)(\mathbf{x}) = \sum_{j=1}^{N} \left(\int_{\mathbb{R}^3} \frac{\overline{\varphi_j(\mathbf{y})} u(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|}\, \mathrm{d}\mathbf{y} \right) \varphi_j(\mathbf{x}). \tag{17}$$

The equations (14) are called the *self-consistent Hartree–Fock equations*. If Ψ is a minimizer for the problem (7)–(8), then Ψ can be written as $\Psi = |\varphi_1 \dots \varphi_N\rangle$ with the φ_i's solving (14), with $\varepsilon_1 \leqslant \varepsilon_2 \leqslant \cdots \leqslant \varepsilon_N < 0$ being the N lowest eigenvalues of the operator h_φ [23].

Remark 1.1. We note that Hartree originally [13] studied the simpler equations

$$(-\Delta + V)\varphi_i(\mathbf{x}) + \left(\sum_{j\neq i} \int_{\mathbb{R}^3} \frac{|\varphi_j(\mathbf{y})|^2}{|\mathbf{x} - \mathbf{y}|}\, \mathrm{d}\mathbf{y} \right) \varphi_i(\mathbf{x}) = \varepsilon_i \varphi_i(\mathbf{x}), \qquad 1 \leqslant i \leqslant N, \tag{18}$$

called the *Hartree equations* (H equations). He derived these without going through a minimization in the variational principle, a refinement which is due to Slater [28]: ignoring the Pauli principle, (18) are the Euler–Lagrange equations for minimizing the functional

$$\mathcal{E}^H(u_1, \dots, u_N) = \mathfrak{q}(\Psi, \Psi) \tag{19}$$

(with $\mathfrak{q}$ as in (3)) over wavefunctions Ψ of the form

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \prod_{i=1}^{N} u_i(\mathbf{x}_i), \qquad u_i \in W^{1,2}(\mathbb{R}^3). \tag{20}$$

Fock [5] and Slater [28] then independently realized how to introduce the Pauli principle (by using Ψ's of the form in (6)), which led to the Hartree–Fock equations in (13).

In the *multiconfiguration self-consistent field method* (MC-SCF) one aims to recover more generality on the wavefunction Ψ by minimizing $\mathfrak{q}(\Psi, \Psi)$ in (3) on *finite sums* of Slater determinants (see (6)) instead of only on a single Slater determinant as in Hartree–Fock theory. More precisely, for $M \geqslant N$, $M, N \in \mathbb{N}$, the set of admissible wavefunctions is limited to Ψ's

which are linear combinations of Slater determinants of length N, built out of M orbitals. The minimization problem then becomes

$$E_M^{\mathrm{MCSCF}}(N,Z) = \inf\left\{\mathfrak{q}(\Psi,\Psi) \;\middle|\; \Psi \in \mathcal{S}_N^M\right\}, \tag{21}$$

$$\mathcal{S}_N^M = \Bigg\{\Psi = \sum_{I=\{i_1<i_2<\cdots<i_N\}\subset\{1,\ldots,M\}} c_I \,|\, u_{i_1}\ldots u_{i_N}\rangle \;|\; u_i \in W^{1,2}(\mathbb{R}^3),$$
$$(u_i,u_j)=\delta_{ij}, c_I\in\mathbb{C}, \sum_I |c_I|^2 = 1\Bigg\}. \tag{22}$$

Note that $\mathcal{S}_N = \mathcal{S}_N^N \subset \mathcal{S}_N^M$, $M \geqslant N$ (see (8)). Also, clearly

$$E^{\mathrm{HF}}(N,Z) = E_N^{\mathrm{MCSCF}}(N,Z) \geqslant E_M^{\mathrm{MCSCF}}(N,Z) \geqslant E^{\mathrm{QM}}(N,Z). \tag{23}$$

In fact, strict inequality holds also in the last inequality [12].

One can express the energy $\mathfrak{q}(\Psi,\Psi)$ for $\Psi \in \mathcal{S}_N^M$ as a (nonlinear) functional of the c_I's and the u_i's (see [20, (6)]), but since this is somewhat complicated and immaterial for our discussion, we shall refrain from doing so here.

The existence of minimizers (provided $Z > N-1$) for the problem (21)–(22) was proved by Friesecke [11] (and for a related case by Le Bris [17]). The corresponding Euler–Lagrange equations, called the *multiconfiguration equations* (MC equations), are

$$\gamma_i(-\Delta+V)\varphi_i + \sum_{j,k,\ell=1}^{M}\left(A_{ijk\ell}\int_{\mathbb{R}^3}\frac{\varphi_k(\mathbf{y})\overline{\varphi_\ell(\mathbf{y})}}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{y}\right)\varphi_j = \sum_{j=1}^{M}\lambda_{ij}\varphi_j, \qquad 1\leqslant i\leqslant M, \tag{24}$$

$$\sum_{J=\{j_1<j_2<\cdots<j_N\}\subset\{1,\ldots,M\}} H_{IJ}c_J = Ec_I, \qquad I=\{i_1<i_2<\cdots<i_N\}\subset\{1,\ldots,M\}. \tag{25}$$

The first equation (24) is a system of M nonlinear partial differential equations. They are the Euler–Lagrange equations for the φ_i's . Here, the coefficients $\gamma_i > 0$ and $A_{ijk\ell} \in \mathbb{C}$ are explicit functions of the c_I's, and the λ_{ij}'s are the Lagrange multipliers of the orthonormality constraints on the φ_i's in (22). The second equation (25) is an eigenvalue problem—the Euler–Lagrange equations for c_I. Here, the coefficients H_{IJ} in the equations for the c_I's are explicit functions of the φ_i's, and E is the Lagrange multiplier of the normalization condition for the c_I's in (22). The details of this are immaterial for our discussion; we refer to [20, 11]. For a derivation of these equations, see [11, appendix 1].

As in the case of the Hartree–Fock equations, equations (24) and (25) can be written in a more compact form as

$$((-\Delta+V)\Gamma + W_\Phi)\cdot\Phi = \Lambda\cdot\Phi, \tag{26}$$

$$H_\Phi\cdot c = Ec, \tag{27}$$

where $\Phi = (\varphi_1,\ldots,\varphi_M)^T$ and $c=(c_I)\in\mathbb{R}^{\binom{M}{N}}$. Here, $\Lambda=(\lambda_{ij})_{1\leqslant i,j\leqslant M}$, and Γ and W_Φ are $M\times M$ matrices (Γ constant, W_Φ dependent on $\mathbf{x}\in\mathbb{R}^3$), given in terms of the γ_i's and the $A_{ijk\ell}$'s in (24) and (25). Again, we refer to [20] for more details.

The existence of saddle points, i.e., an infinite sequence

$$\{c_n, \boldsymbol{\varphi}_n\}_{n\in\mathbb{N}} = \left\{(c_I)_n; \{\varphi_1^n,\ldots,\varphi_M^n\}\right\}_{n\in\mathbb{N}}$$

of solutions to (24) and (25) was proved by Lewin [20] (again, provided $Z > N-1$).

A natural mathematical question is to study the regularity properties of solutions to the multiconfiguration equations (including the Hartree–Fock equations). However, this question is also of practical interest, since regularity properties of the solutions have influence on the convergence properties of various numerical schemes. We refer to [18, 19] for discussions on this.

It was proved in [23, theorem 3.2] that if $\varphi = \{\varphi_1, \ldots, \varphi_N\}$ is a solution of the Hartree–Fock equations (14), then the φ_i's are globally Lipschitz continuous, i.e., $\varphi_i \in C^{0,1}(\mathbb{R}^3)$. This also holds for solutions to the Hartree equations [23, theorem 3.1] (see also [23, *remarks* (4), p 192]). The proof readily extends to solutions of the multiconfiguration equations. Note also that it was proved in [24] (for HF) and in [20] (for MC) that the φ_i's belong to $W^{2,p}(\mathbb{R}^3)$ for all $p \in [2, 3)$ and consequently, by the Sobolev inequality [2, theorem 6 (ii)], to $C^\alpha(\mathbb{R}^3)$ for all $\alpha \in (0, 1)$.

Furthermore, the φ_i's are real analytic away from the positions of the nuclei, i.e., $\varphi_i \in C^\omega(\mathbb{R}^3 \backslash \{R_1, \ldots, R_L\})$. This was first proved in (the preprint version of) [20], for solutions to the multiconfiguration equations (24)–(25) (see also [12]); it was conjectured in [23], where smoothness ($\varphi_i \in C^\infty(\mathbb{R}^3 \backslash \{R_1, \ldots, R_L\})$) was proved. Note also that if $\varphi = \{\varphi_1, \ldots, \varphi_N\}$ is a solution to (14) and if $\tilde{\varphi}$ satisfies $h_\varphi \tilde{\varphi} = \varepsilon \tilde{\varphi}$, then $\tilde{\varphi}$ has the same regularity properties as those of the φ_i's discussed above.

The main result of this paper is the following theorem, which completely settles the regularity properties at the positions $R_1, \ldots, R_L$ of the nuclei of all solutions to the multiconfiguration equations (24)–(25) (including the Hartree–Fock equations (13)). We denote by $B_3(R, r) \subset \mathbb{R}^3$ the ball of radius $r > 0$ with center at $R \in \mathbb{R}^3$.

Theorem 1.2. *Let* $\{(c_I); \{\varphi_1, \ldots, \varphi_M\}\}$ *be a solution to the multiconfiguration equations (24)–(25).*

Then, for all $j \in \{1, \ldots, M\}$ *and* $k \in \{1, \ldots, L\}$, *there exist* $r \equiv r_{j,k} > 0$ *and real analytic functions* $\varphi^{(1)}_{j,k}, \varphi^{(2)}_{j,k} : B_3(R_k, r) \to \mathbb{C}$, *i.e.,* $\varphi^{(1)}_{j,k}, \varphi^{(2)}_{j,k} \in C^\omega(B_3(R_k, r))$, *such that*

$$\varphi_j(\mathbf{x}) = \varphi^{(1)}_{j,k}(\mathbf{x}) + |\mathbf{x} - R_k| \varphi^{(2)}_{j,k}(\mathbf{x}), \qquad \mathbf{x} \in B_3(R_k, r). \tag{28}$$

Remark 1.3.

(i) For simplicity of notation, we have stated everything only in the spinless case. It will be obvious that the proof of theorem 1.2 also works in the general case of spin q. It will also be clear that the result also holds for solutions to the Hartree equations (18).

(ii) The result of theorem 1.2 immediately implies regularity results for the many-body wavefunction Ψ generated by (c_I) and $\{\varphi_1, \ldots, \varphi_M\}$ (see (22)). For recent results on the regularity properties of the *true* minimizer Ψ (i.e., for the problem (4)) and of excited states, we refer to [8, 9]. The proof of theorem 1.2 uses the Kustaanheimo–Stiefel transformation, as applied in [9] to study these eigenfunctions of the Schrödinger operator of atoms and molecules (i.e., solutions to (5)) near two-particle coalescence points.

Remark 1.4. Partial results on the *asymptotic* regularity at the positions of the nuclei of solutions to Hartree–Fock equations have recently been given in [4]; more precisely, the estimates of the form

$$\left|\partial^\beta_{\mathbf{x}} \varphi_j(\mathbf{x})\right| \leqslant C_{j,k,\beta,\varepsilon_{j,k}} |\mathbf{x} - R_k|^{1-|\beta|}, \tag{29}$$

for $|\beta| \geqslant 1$ and $\mathbf{x} \in B_3(R_k, \varepsilon_{j,k})$ for some $\varepsilon_{j,k} > 0$, were proved to hold for *certain* solutions to the Hartree–Fock equations obtained by the so-called *level-shifting algorithm* [1]. We shall not discuss this in detail here, but just point out that theorem 1.2 implies that *any* solution to the Hartree–Fock equations (and, more generally, to the multiconfiguration equations) satisfies

the estimate (29). This fact is relevant for the study in [3] of the use of tensor product wavelets in the approximation of Hartree–Fock eigenfunctions. The result of theorem 1.2 is, however, much stronger than (29).

Theorem 1.2 immediately implies similar regularity properties for the corresponding (electron) *density*. More precisely, for $\Psi \in L^2(\mathbb{R}^{3N})$, define $\rho \equiv \rho_\Psi$ by (recall that $\mathbf{X} = (\mathbf{x}_1, \ldots, \mathbf{x}_N) \in \mathbb{R}^{3N}$)

$$\rho(\mathbf{x}) = \sum_{j=1}^{N} \int_{\mathbb{R}^{3N}} |\Psi(\mathbf{X})|^2 \delta(\mathbf{x} - \mathbf{x}_j)\, \mathrm{d}\mathbf{X}. \tag{30}$$

For $\Psi \in \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3)$, this becomes

$$\rho(\mathbf{x}) = N \int_{\mathbb{R}^{3N-3}} |\Psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2\, \mathrm{d}\mathbf{x}_2 \cdots \mathrm{d}\mathbf{x}_N. \tag{31}$$

For Ψ a Slater determinant, ρ is given in (10); for Ψ a *product state* (see (20)), ρ is also given by (10), whereas for Ψ a linear combination of Slater determinants of length N, built out of M functions (see (22)), ρ becomes

$$\rho(\mathbf{x}) = \sum_{j=1}^{M} n_j |\varphi_j(\mathbf{x})|^2, \qquad n_j = \sum_{I \ni j} {c_I}^2. \tag{32}$$

Since, for any solution of (24) and (25), the orbitals are real analytic away from the positions of the nuclei, the same holds for the corresponding density ρ (i.e., $\rho \in C^\omega(\mathbb{R}^3 \backslash \{R_1, \ldots, R_L\})$), defined by (32) (since these are *finite* sums). The following corollary to theorem 1.2 completely settles the regularity properties of ρ at the positions $R_1, \ldots, R_L$ of the nuclei.

Corollary 1.5. *Let $\{(c_I); \{\varphi_1, \ldots, \varphi_M\}\}$ be a solution to the multiconfiguration equations (24)–(25), and let ρ be the corresponding electron density, given by (32).*

Then for all $k \in \{1, \ldots, M\}$ there exist $r_k > 0$ and real analytic functions $\rho_1, \rho_2 : B_3(R_k, r_k) \to \mathbb{R}$ (i.e., $\rho_1, \rho_2 \in C^\omega(B_3(R_k, r_k))$), such that

$$\rho(\mathbf{x}) = \rho_1(\mathbf{x}) + |\mathbf{x} - R_k| \rho_2(\mathbf{x}) \qquad \textit{for all} \quad \mathbf{x} \in B_3(R_k, r_k). \tag{33}$$

Remark 1.6. Note that the corresponding question for the density ρ (given by (31)) of the *true* minimizer of (4) as well as of excited states—i.e., solutions to (5)—remains open. In this case, the density is known to be real analytic away from the positions of the nuclei (i.e., $\rho \in C^\omega(\mathbb{R}^3 \backslash \{R_1, \ldots, R_L\})$) (see [7]), and partial results on the behavior in the vicinity of the nuclei were obtained in [6, 10].

2. Proof of the main theorem

As mentioned in section 1, the proof of theorem 1.2 is based on the Kustaanheimo–Stiefel (KS) transform. We will 'lift' the multiconfiguration equations (24) to new coordinates using that transform. The solutions to the new equations will be real analytic functions. By projecting to the original coordinates, we get the structure result in theorem 1.2. The latter fact was proved in [9] (see proposition 2.1 below).

The KS transform $K : \mathbb{R}^4 \to \mathbb{R}^3$ is defined by

$$K(\mathbf{y}) = \begin{pmatrix} y_1^2 - y_2^2 - y_3^2 + y_4^2 \\ 2(y_1 y_2 - y_3 y_4) \\ 2(y_1 y_3 + y_2 y_4) \end{pmatrix}, \qquad \mathbf{y} = (y_1, y_2, y_3, y_4) \in \mathbb{R}^4. \tag{34}$$

It is a simple computation to verify that

$$|K(\mathbf{y})| := \|K(\mathbf{y})\|_{\mathbb{R}^3} = \|\mathbf{y}\|_{\mathbb{R}^4}^2 =: |\mathbf{y}|^2 \qquad \text{for all} \quad \mathbf{y} \in \mathbb{R}^4. \tag{35}$$

Let $f : \mathbb{R}^3 \to \mathbb{C}$ be any C^2-function, and define, with K as above,

$$f_K : \mathbb{R}^4 \to \mathbb{C}, \qquad f_K(\mathbf{y}) := f(K(\mathbf{y})). \tag{36}$$

Then for all $\mathbf{y} \in \mathbb{R}^4 \backslash \{0\}$, (see [9, lemma 3.1]),

$$(\Delta f)(K(\mathbf{y})) = \frac{1}{4|\mathbf{y}|^2} \Delta f_K(\mathbf{y}). \tag{37}$$

Proof of theorem 1.2. We prove the theorem in the case $k = 1$. We assume without loss of generality (make a linear transformation in $\mathbb{R}^3$) that $R_1 \equiv 0 \in \mathbb{R}^3$.

Assume that $\{(c_I); \{\varphi_1, \ldots, \varphi_M\}\}$ solves the multiconfiguration equations (24)–(25). Define

$$\phi_{k,\ell} := (\varphi_k \overline{\varphi_\ell}) * \frac{1}{|\cdot|}, \qquad k, \ell \in \{1, \ldots, N\}. \tag{38}$$

Then (24) can be rewritten as

$$\gamma_i(-\Delta_{\mathbf{x}} + V)\varphi_i + \sum_{j,k,\ell=1}^{M} A_{ijk\ell}\phi_{k,\ell}\varphi_j = \sum_{j=1}^{M} \lambda_{ij}\varphi_j, \qquad 1 \leqslant i \leqslant M, \tag{39}$$

$$-\Delta_{\mathbf{x}}\phi_{k,\ell} = 4\pi\varphi_k\overline{\varphi_\ell}, \qquad 1 \leqslant k, \ell \leqslant M. \tag{40}$$

Since $V(\mathbf{x}) = -\sum_{k=1}^{L} Z_k|\mathbf{x} - R_k|^{-1}$ is real analytic on $\mathbb{R}^3\backslash\{R_1, \ldots, R_L\}$, (39) and (40) show that $\{\varphi_i, \phi_{k,\ell}\}_{i,k,\ell}$ is a solution of an analytic nonlinear elliptic system of PDEs on $\mathbb{R}^3\backslash\{R_1, \ldots, R_L\}$. It follows (from [25, 26] or the method in [15]) that $\{\varphi_i\}_{i=1,\ldots,M}$ and $\{\phi_{k,\ell}\}_{1\leqslant k,\ell\leqslant M}$ are real analytic in $\mathbb{R}^3\backslash\{R_1, \ldots, R_L\}$. This is the standard proof that solutions to the multiconfiguration equations (24)–(25) are real analytic away from the origin in $\mathbb{R}^3$ [12, 20].

Recall that $R_1 = 0 \in \mathbb{R}^3$. Note that (39)–(40), (37) and (35) imply that

$$\gamma_i(-\Delta_{\mathbf{y}} + 4|\mathbf{y}|^2 V_K)(\varphi_i)_K + \sum_{j,k,\ell=1}^{M} A_{ijk\ell} 4|\mathbf{y}|^2 (\phi_{k,\ell})_K (\varphi_j)_K - 4|\mathbf{y}|^2 \sum_{j=1}^{M} \lambda_{ij}(\varphi_j)_K = 0,$$
$$1 \leqslant i \leqslant M, \tag{41}$$

$$-\Delta_{\mathbf{y}}(\phi_{k,\ell})_K = 16\pi|\mathbf{y}|^2(\varphi_k)_K(\overline{\varphi_\ell})_K, \qquad 1 \leqslant k, \ell \leqslant M, \tag{42}$$

with V_K, $(\varphi_i)_K$ and $(\phi_{k,\ell})_K$ defined by (36).

Since the functions involved do not have sufficient regularity for (37) to be applied directly, the above deduction of (41)–(42) is slightly incomplete. One can make a rigorous proof using lemma A.1 and remark A.2 in appendix A. This was carried out in [9, pp 6–7] in a similar setting, and details are therefore omitted here.

Since (using (35))

$$4|\mathbf{y}|^2 V_K(\mathbf{y}) = -4Z_1 - \sum_{k=2}^{L} \frac{4Z_k|\mathbf{y}|^2}{|K(\mathbf{y}) - R_k|} \tag{43}$$

is real analytic in a neighborhood of $0 \in \mathbb{R}^3$ (recall (35)), (41) and (42) show that

$$\{(\varphi_i)_K, (\phi_{k,\ell})_K\}_{1\leqslant i,k,\ell\leqslant M} \tag{44}$$

is a solution of an analytic nonlinear elliptic system of PDEs on some ball $B_4(0, R) \subset \mathbb{R}^4$. As before, it follows that

$$\{(\varphi_i)_K\}_{1\leqslant i\leqslant M} \qquad \text{and} \qquad \{(\phi_{k,\ell})_K\}_{1\leqslant k,\ell\leqslant M} \tag{45}$$

are real analytic in $B_4(0, R) \subset \mathbb{R}^4$. Proposition 2.1 below, proved in [9], then implies the statement of theorem 1.2. This finishes the proof of the theorem. □

Proposition 2.1 ([9, proposition 4.1])**.** *Let $U \subset \mathbb{R}^3$ be open with $0 \in U$ and let $\varphi : U \to \mathbb{C}$ be a function. Let $\mathcal{U} = K^{-1}(U) \subset \mathbb{R}^4$, with $K : \mathbb{R}^4 \to \mathbb{R}^3$ from (34), and suppose that*

$$\varphi_K = \varphi \circ K : \mathcal{U} \to \mathbb{C} \tag{46}$$

is real analytic.

Then there exist functions $\varphi^{(1)}, \varphi^{(2)}$, real analytic in a neighborhood of $0 \in \mathbb{R}^3$, such that

$$\varphi(\mathbf{x}) = \varphi^{(1)}(\mathbf{x}) + |\mathbf{x}|\varphi^{(2)}(\mathbf{x}). \tag{47}$$

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Appendix. The Kustaanheimo–Stiefel transform

The KS transform turns out to be a very useful and natural tool for the investigation of Schrödinger equations with Coulombic interactions (we refer to [9] for references on this). In particular (35) and the following lemma are important for our proofs. Most of the facts stated here are well known (see e.g. [14, appendix A]).

Lemma A.1 ([9, lemma 3.1])**.** *Let $K : \mathbb{R}^4 \to \mathbb{R}^3$ be defined as in (34), let $f : \mathbb{R}^3 \to \mathbb{C}$ be any C^2-function, and define $f_K : \mathbb{R}^4 \to \mathbb{C}$ by (36).*

(a) Then (37) holds:

$$(\Delta f)(K(\mathbf{y})) = \frac{1}{4|\mathbf{y}|^2}\Delta f_K(\mathbf{y}), \qquad \mathbf{y} \in \mathbb{R}^4 \setminus \{0\}. \tag{A.1}$$

(b) Furthermore, let $U = B_3(0, r) \subset \mathbb{R}^3$ for $r \in (0, \infty]$. Then, for $\phi \in C_0(\mathbb{R}^3)$ (continuous with compact support),

$$\int_{K^{-1}(U)} |\phi(K(\mathbf{y}))|^2 \, \mathrm{d}\mathbf{y} = \frac{\pi}{4}\int_U \frac{|\phi(\mathbf{x})|^2}{|\mathbf{x}|}\, \mathrm{d}\mathbf{x}. \tag{A.2}$$

In particular,

$$\| |\mathbf{y}|\phi_K \|^2_{L^2(K^{-1}(U))} = \frac{\pi}{4}\|\phi\|^2_{L^2(U)}. \tag{A.3}$$

Remark A.2 ([9, remark 3.2])**.** By a density argument, the isometry (A.3) allows us to extend the composition by K given by (36) (the pull-back K^* by K) to a map

$$K^* : L^2(U, \mathrm{d}\mathbf{x}) \to L^2(K^{-1}(U), \frac{4}{\pi}|\mathbf{y}|^2\,\mathrm{d}\mathbf{y})$$
$$\phi \mapsto \phi_K$$

in the case when $U = B_3(0, r), r \in (0, \infty]$. This makes ϕ_K well-defined for any $\phi \in L^2(U)$. Furthermore, if $\phi_n \to \phi$ in $L^2(U)$, then, for all $g \in C^\infty(K^{-1}(U))$ ($g \in C_0^\infty(K^{-1}(U))$, if $r = \infty$),

$$\lim_{n\to\infty} \int_{K^{-1}(U)} g(\mathbf{y})(\phi_n)_K(\mathbf{y})\,\mathrm{d}\mathbf{y} = \int_{K^{-1}(U)} g(\mathbf{y})\phi_K(\mathbf{y})\,\mathrm{d}\mathbf{y}. \tag{A.4}$$

This follows from Schwarz' inequality and (A.3),

$$\begin{aligned}
&\left|\int_{K^{-1}(U)} g(\mathbf{y})((\phi_n)_K(\mathbf{y}) - \phi_K(\mathbf{y}))\,\mathrm{d}\mathbf{y}\right| \\
&\quad\leqslant \left(\int_{K^{-1}(U)} \frac{|g(\mathbf{y})|^2}{|\mathbf{y}|^2}\,\mathrm{d}\mathbf{y}\right)^{1/2} \|\,|\mathbf{y}|((\phi_n)_K - \phi_K)\|_{L^2(K^{-1}(U))} \\
&\quad= \frac{\sqrt{\pi}}{2}\left(\int_{K^{-1}(U)} \frac{|g(\mathbf{y})|^2}{|\mathbf{y}|^2}\,\mathrm{d}\mathbf{y}\right)^{1/2} \|\phi_n - \phi\|_{L^2(U)} \to 0, \qquad n \to \infty.
\end{aligned}$$

Here the $\mathbf{y}$-integral clearly converges since $g \in C^\infty(\mathbb{R}^4)$ ($g \in C_0^\infty(\mathbb{R}^4)$, if $r = \infty$).

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