Analytic structure of solutions to multiconfiguration equations
Fournais, Søren; Hoffmann-Ostenhof, Maria; Hoffmann-Ostenhof, Thomas; Sørensen, Thomas Østergaard

Publication date:
2008

Document Version
Publisher's PDF, also known as Version of record

Link to publication from Aalborg University

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

? Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
? You may not further distribute the material or use it for any profit-making activity or commercial gain
? You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us at vbn@aub.aau.dk providing details, and we will remove access to the work immediately and investigate your claim.
Analytic structure of solutions to multiconfiguration equations

by

S. Fournais, M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof and T. Østergaard Sørensen

R-2008-20 December 2008
ANALYTIC STRUCTURE OF SOLUTIONS TO MULTICONFIGURATION EQUATIONS

S. FOURNAIS, M. HOFFMANN-OSTENHOF, T. HOFFMANN-OSTENHOF, AND T. OSTERGAARD SØRENSEN

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 neighbourhood \( U_{j,k} \subseteq \mathbb{R}^3 \) of \( R_k \), and functions \( \varphi_{j,k}^{(1)}, \varphi_{j,k}^{(2)} \), real analytic in \( U_{j,k} \), such that
\[
\varphi_j(x) = \varphi_{j,k}^{(1)}(x) + |x - R_k| \varphi_{j,k}^{(2)}(x), \quad x \in U_{j,k}.
\]
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.

1. Introduction and results

We consider the Hamiltonian of a molecule with \( N \) non-relativistic electrons and \( L \) (static) nuclei of (positive) charges \( Z_1, \ldots, Z_L \), fixed at \( R_1, \ldots, R_L \in \mathbb{R}^3 \), given by
\[
H = H(N, Z) = \sum_{j=1}^{N} \left\{-\Delta_j + V(x_j)\right\} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|},
\]
\[
V(x) = -\sum_{k=1}^{L} \frac{Z_k}{|x - R_k|}.
\]
Here, \( x_j \in \mathbb{R}^3 \) is the coordinate of the \( j \)’th electron and \( \Delta_j \) is the Laplacian with respect to \( x_j \). 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

Date: December 9, 2008.

© 2008 by the authors. This article may be reproduced, in its entirety, for non-commercial purposes.
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 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 \( q \) be the quadratic form defined by \( H \), that is, for \( \Psi \in \mathcal{D}(H) \),
\[
q(\Psi, \Psi) = \langle \Psi, H\Psi \rangle.
\]

Then, for \( \Psi \in \mathcal{Q}(H) \), (with \( X = (x_{1}, \ldots, x_{N}) \in \mathbb{R}^{3N} \))
\[
q(\Psi, \Psi) = \sum_{j=1}^{N} \int_{\mathbb{R}^{3N}} |\nabla_{j}\Psi(X)|^{2} dX
+ \int_{\mathbb{R}^{3N}} \left\{ \sum_{j=1}^{N} V(x_{j}) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_{i} - x_{j}|} \right\} |\Psi(X)|^{2} dX.
\]

Here, \( \nabla_{j} \) is the gradient with respect to \( x_{j} \), and \( \langle , \rangle \) is the scalar product in \( \mathcal{H}_{F} \subset L^{2}(\mathbb{R}^{3N}) \). The quadratic form \( q \) is bounded from below. The quantum ground state energy is the infimum of this quadratic form:
\[
E^{QM}(N, Z) := \inf_{\sigma_{\mathcal{H}_{F}}(H)} \inf_{\sigma_{\mathcal{H}_{F}}(H)} q(\Psi, \Psi).
\]

The Euler–Lagrange equation for the minimization problem (4) is nothing but the (stationary) Schrödinger equation,
\[
H \Psi = E\psi, \quad \Psi \in \mathcal{D}(H),
\]
with \( E \equiv E^{QM}(N, Z) \). A ground state of the atom is a solution to (5) for \( E = E^{QM}(N, Z) \); excited states of the atom are solutions to (5) with \( E > E^{QM}(N, Z) \). Zhilin [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 $q$ in the entire (linear) $N$-particle space $\mathcal{H}_F$ (or rather, $\mathcal{Q}(H)$), one restricts to wavefunctions $\Psi$ which are pure wedge products, also called Slater determinants:

$$\Psi(x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}} \det(u_i(x_j))_{i,j=1}^N \equiv |u_1 \ldots u_N\rangle(x_1, \ldots, x_N),$$

with $\{u_i\}_{i=1}^N \subset W^{1,2}(\mathbb{R}^3)$, orthonormal in $L^2(\mathbb{R}^3)$ (called orbitals). Notice 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 $q$ defined by $H$ over such Slater determinants:

$$E_{HF}(N, Z) := \inf \{ q(\Psi, \Psi) \mid \Psi \in \mathcal{S}_N \},$$

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

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

$$E_{HF}(u_1, \ldots, u_N) := q(\Psi, \Psi)$$

$$= \sum_{j=1}^N \int_{\mathbb{R}^3} \left\{ |\nabla u_j(x)|^2 + V(x)|u_j(x)|^2 \right\} dx$$

$$+ \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dxdy - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\gamma(x,y)^2}{|x-y|} dxdy,$$

where $\rho$ is the density and $\gamma$ is the density matrix of $\Psi$, given by

$$\gamma(x,y) = \sum_{i=1}^N u_i(y) u_i(x), \quad \rho(x) = \gamma(x,x) = \sum_{i=1}^N |u_i(x)|^2.$$

With $E_{HF}$ defined this way, the minimization problem (7)–(8) can be formulated as

$$E_{HF}(N, Z) = \inf \{ E_{HF}(u_1, \ldots, u_N) \mid (u_1, \ldots, u_N) \in \mathcal{M}_N \},$$

$$\mathcal{M}_N = \{ (u_1, \ldots, u_N) \in [W^{1,2}(\mathbb{R}^3)]^N \mid (u_i, u_j) = \delta_{ij} \}.$$
was first proved by Lieb and Simon [23]. The Euler–Lagrange equations of the problem (11)–(12) are the Hartree–Fock equations (HF–equations),

\[
(−\Delta + V)\varphi_i(x) + \left( \sum_{j=1}^{N} \int_{\mathbb{R}^3} \frac{|\varphi_j(y)|^2}{|x−y|} \, dy \right) \varphi_i(x)
\]

\[− \sum_{j=1}^{N} \left( \int_{\mathbb{R}^3} \frac{\varphi_j(y)\varphi_i(y)}{|x−y|} \, dy \right) \varphi_j(x) = \varepsilon_i \varphi_i(x), \quad 1 \leq i \leq N.
\]

Here, the \(\varepsilon_i\)'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 \(\mathcal{E}_{HF}\) in (9) and the orthogonality constraints in (12) are invariant under unitary transformations (that is, if \((u_1, \ldots, u_N) \in \mathcal{M}_N\) and \((\tilde{u}_1, \ldots, \tilde{u}_N) = U(u_1, \ldots, u_N)\) for \(U\) an \(N \times N\) unitary matrix, then \(\mathcal{E}_{HF}(\tilde{u}_1, \ldots, \tilde{u}_N) = \mathcal{E}_{HF}(u_1, \ldots, u_N)\) and \((\tilde{u}_1, \ldots, \tilde{u}_N) \in \mathcal{M}_N\), the matrix of Lagrange multipliers due to (12) may be diagonalised without loss of generality, which turns the Euler–Lagrange equations into (13).

In [23] it was also proved that if \((\varphi_1, \ldots, \varphi_N) \in \mathcal{M}_N\) is a minimizer of the problem (11)–(12) then \(\{\varphi_1, \ldots, \varphi_N\}\) 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 \(\{\varphi_n\}_{n \in \mathbb{N}} = \{\varphi_1^n, \ldots, \varphi_N^n\}_{n \in \mathbb{N}}\) 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

\[h\varphi_i = \varepsilon_i \varphi_i , \quad 1 \leq i \leq N ,
\]

with \(h\varphi\) the Hartree–Fock operator associated to \(\varphi = \{\varphi_1, \ldots, \varphi_N\}\), given by

\[h\varphi u = (−\Delta + V)u + R_\varphi u − K_\varphi u ,
\]

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

\[R_\varphi(x) := \sum_{j=1}^{N} \int_{\mathbb{R}^3} \frac{|\varphi_j(y)|^2}{|x−y|} \, dy
\]

and \(K_\varphi u\) is the exchange term, given by the integral operator

\[(K_\varphi u)(x) = \sum_{j=1}^{N} \left( \int_{\mathbb{R}^3} \frac{\varphi_j(y)u(y)}{|x−y|} \, dy \right) \varphi_j(x) .
\]
The equations (14) are called the self-consistent Hartree-Fock equations. If \( \Psi \) is a minimizer for the problem (7)–(8), then \( \Psi \) can be written as \( \Psi = |\varphi_1 \ldots \varphi_N \rangle \) with the \( \varphi_i \)'s solving (14), with \( \varepsilon_1 \leq \varepsilon_2 \leq \cdots \leq \varepsilon_N < 0 \) the \( N \) lowest eigenvalues of the operator \( h_{\varphi} \) [23].

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

\[
( - \Delta + V) \varphi_i (x) + \left( \sum_{j \neq i} \int_{\mathbb{R}^3} \frac{|\varphi_j (y)|^2}{|x - y|} \, dy \right) \varphi_i (x) = \varepsilon_i \varphi_i (x) , \quad 1 \leq i \leq N ,
\]

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

\[
\mathcal{E}^H (u_1 , \ldots , u_N) = q(\Psi, \Psi) \quad (19)
\]

over wavefunctions \( \Psi \) of the form

\[
\Psi (x_1 , \ldots , x_N) = \prod_{i=1}^{N} u_i (x_i) , \quad u_i \in W^{1,2}(\mathbb{R}^3) . \quad (20)
\]

Fock [5] and Slater [28] then independently realised how to introduce the Pauli principle (by using \( \Psi \)'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 \( \Psi \) by minimizing \( q(\Psi, \Psi) \) in (3) on finite sums of Slater determinants (see (6)) instead of only on a single Slater determinant as in Hartree–Fock theory (of course any \( \Psi \in \mathcal{Q}(H) \) is an infinite sum of Slater determinants). More precisely, for \( M \geq N, M, N \in \mathbb{N} \), the set of admissible wavefunctions is limited to the \( \Psi \)'s which are linear combinations of Slater determinants of length \( N \), built out of \( M \) orbitals. The minimization problem then becomes

\[
E^\text{MCSCF}_M (N, Z) = \inf \{ q(\Psi, \Psi) \mid \Psi \in \mathcal{S}^M_N \} , \quad (21)
\]

\[
\mathcal{S}^M_N = \{ \Psi = \sum_{I=\{i_1 < i_2 < \cdots < i_N \} \subset \{1, \ldots , M \}} c_I |u_{i_1} \ldots u_{i_N} \rangle \mid u_i \in W^{1,2}(\mathbb{R}^3) , \quad (22)
\]

\[
(u_i, u_j) = \delta_{ij} , \quad c_I \in \mathbb{C} , \quad \sum_I |c_I|^2 = 1 \} .
\]
Note that $S_N = S_N^N \subset S_N^M$, $M \geq N$ (see (8)). Also, clearly

$$E^{\text{HF}}(N, Z) = E^{\text{MCSCF}}_N(N, Z) \geq E^{\text{MCSCF}}_M(N, Z) \geq E^{\text{QM}}(N, Z).$$

(23)

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

One can express the energy $q(\Psi, \Psi)$ for $\Psi \in S^M_N$ 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

$$\gamma_i \left(-\Delta + V\right) \varphi_i + \sum_{j,k,\ell=1}^M \left(A_{ijk\ell} \int_{\mathbb{R}^3} \frac{\varphi_k(y) \varphi_\ell(y)}{|x-y|} dy\right) \varphi_j = \sum_{j=1}^M \lambda_{ij} \varphi_j, \quad 1 \leq i \leq M,$$

(24)

$$\sum_{J=\{j_1 < j_2 < \cdots < j_N\} \subset \{1, \ldots, M\}} H_{IJ} c_J = E c_I, \quad I = \{i_1 < i_2 < \cdots < i_N\} \subset \{1, \ldots, M\}.$$  

(25)

The first equation (24) is a system of $M$ nonlinear partial differential equations. They are the Euler–Lagrange equations for the $\varphi_i$’s. Here, the coefficients $\gamma_i > 0$ and $A_{ijk\ell} \in \mathbb{C}$ are explicit functions of the $c_I$’s, and the $\lambda_{ij}$’s are Lagrange multipliers of the orthonormality constraints on the $\varphi_i$’s in (22). The second equation (25) is an eigenvalue problem—the Euler–Lagrange equations for the $c_I$. Here, the coefficients $H_{IJ}$ in the equations for the $c_I$’s are explicit functions of the $\varphi_i$’s, and $E$ is the Lagrange multiplier of the normalisation 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, the equations (24)–(25) can be written in a more compact form:

$$(( -\Delta + V) \Gamma + W_\Phi) \cdot \Phi = \Lambda \cdot \Phi,$$

(26)

$$H_\Phi \cdot c = E c,$$

(27)

where $\Phi = (\varphi_1, \ldots, \varphi_M)^T$ and $c = (c_I) \in \mathbb{R}^M_N$. Here, $\Lambda = (\lambda_{ij})_{1 \leq i, j \leq M}$, and $\Gamma$ and $W_\Phi$ are $M \times M$ matrices ($\Gamma$ constant, $W_\Phi$ dependent on
x ∈ ℝ³), given in terms of the γᵢ’s and the Aᵢᵣᵣᵣbeing’s in (24)–(25). Again, we refer to [20] for more details.

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

\[ \{c_n, \varphi_n\}_{n \in \mathbb{N}} = \{(c_I)_n; \varphi^n_1, \ldots, \varphi^n_M\}_{n \in \mathbb{N}} \]

of solutions to (24)–(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 \( \varphi_i \)'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 \( \varphi_i \)'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 \( \varphi_i \)'s are real analytic away from the positions of the nuclei, i.e., \( \varphi_i \in C^\omega(\mathbb{R}^3 \setminus \{R_1, \ldots, R_L\}) \). 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 (\( \varphi_i \in C^\infty(\mathbb{R}^3 \setminus \{R_1, \ldots, R_L\}) \)) was proved. Note also that if \( \varphi = \{\varphi_1, \ldots, \varphi_N\} \) is a solution to (14), and if \( \varphi \) satisfies \( h_\varphi \varphi = \varepsilon \varphi \), then \( \varphi \) has the same regularity properties as those of the \( \varphi_i \)'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 centre 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 \( \varepsilon \equiv \varepsilon_{j,k} > 0 \) and real analytic functions \( \varphi^{(1)}_{j,k}, \varphi^{(2)}_{j,k} : B_3(R_k, \varepsilon) \to \mathbb{C} \), that is,
\( \phi_{j,k}^{(1)}, \phi_{j,k}^{(2)} \in C^\omega(B_3(R_k, \varepsilon)) \), such that
\[
\phi_j(x) = \phi_{j,k}^{(1)}(x) + |x - R_k| \phi_{j,k}^{(2)}(x), \quad x \in B_3(R_k, \varepsilon). \tag{28}
\]

**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 \( \Psi \) generated by \( (c_I) \) and \( \{ \phi_1, \ldots, \phi_M \} \) (see (22)). For recent results on the regularity properties of the true minimizer \( \Psi \) (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 (that is, 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 were recently given in [4]; more precisely, estimates of the form
\[
|\partial^{\beta} \phi_j(x)| \leq C_{j,k,\beta,\varepsilon,j,k} |x - R_k|^{1-|\beta|}, \tag{29}
\]
for \( |\beta| \geq 1 \) and \( x \in B_3(R_k, \varepsilon_{j,k}) \) 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 \( X = (x_1, \ldots, x_N) \in \mathbb{R}^{3N} \))
\[
\rho(x) = \sum_{j=1}^N \int_{\mathbb{R}^{3N}} |\Psi(X)|^2 \delta(x - x_j) \, dX. \tag{30}
\]
For $\Psi \in \bigwedge_{i=1}^{N} L^{2}(\mathbb{R}^{3})$, this becomes

$$\rho(x) = N \int_{\mathbb{R}^{3N-3}} |\Psi(x, x_{2}, \ldots, x_{N})|^{2} \, dx_{2} \cdots dx_{N}. \quad (31)$$

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

$$\rho(x) = \sum_{j=1}^{M} n_{j} |\varphi_{j}(x)|^{2}, \quad n_{j} = \sum_{I \ni j} c_{I}^{2}. \quad (32)$$

Since, for any solution of (24)–(25), the orbitals are real analytic away from the positions of the nuclei, the same holds for the corresponding density $\rho$ (i.e., $\rho \in C^{\omega}(\mathbb{R}^{3} \setminus \{R_{1}, \ldots, R_{L}\})$), defined by (32) (since these are finite sums). The following corollary to Theorem 1.2 completely settles the regularity properties of $\rho$ 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 $\rho$ be the corresponding electron density, given by (32).

Then for all $k \in \{1, \ldots, M\}$ there exist $\varepsilon_{k} > 0$ and real analytic functions $\rho_{1}, \rho_{2} : B_{3}(R_{k}, \varepsilon_{k}) \to \mathbb{R}$ (i.e., $\rho_{1}, \rho_{2} \in C^{\omega}(B_{3}(R_{k}, \varepsilon_{k}))$), such that

$$\rho(x) = \rho_{1}(x) + |x - R_{k}| \rho_{2}(x) \quad \text{for all } x \in B_{3}(R_{k}, \varepsilon_{k}). \quad (33)$$

**Remark 1.6.** Note that the corresponding question for the density $\rho$ (given by (31)) of the true minimizer of (4) as well as of excited states—that is, 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., $\rho \in C^{\omega}(\mathbb{R}^{3} \setminus \{R_{1}, \ldots, R_{L}\})$) (see [7]), and partial results on the behaviour in the vicinity of the nuclei were obtained in [6, 10].

2. **Proof of the main theorem**

As mentioned in the introduction the proof of Theorem 1.2 is based on the Kustaanheimo-Stiefel (KS) transform. We will ‘lift’ the multi-configuration 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

$$K(y) = \begin{bmatrix} y_1^2 - y_2^2 - y_3^2 + y_4^2 \\ 2(y_1y_2 - y_3y_4) \\ 2(y_1y_3 + y_2y_4) \end{bmatrix}, \quad y = (y_1, y_2, y_3, y_4) \in \mathbb{R}^4. \quad (34)$$

It is a simple computation to verify that

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

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

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

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

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

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

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

Then (24) can be rewritten

$$\gamma_i(\Delta_x + V) \varphi_i + \sum_{j,k,\ell=1}^M A_{ijk\ell} \phi_{k,\ell} \varphi_j = \sum_{j=1}^M \lambda_{ij} \varphi_j, \quad 1 \leq i \leq M, \quad (39)$$

$$-\Delta_x \phi_{k,\ell} = 4\pi \varphi_k \overline{\varphi_\ell}, \quad 1 \leq k, \ell \leq M. \quad (40)$$

Since $V(x) = -\sum_{k=1}^L Z_k|x-R_k|^{-1}$ is real analytic on $\mathbb{R}^3 \setminus \{R_1, \ldots, R_L\}$, (39)–(40) shows that $\{\varphi_i, \phi_{k,\ell}\}_{i,k,\ell}$ is a solution of an analytic nonlinear elliptic system of PDE’s on $\mathbb{R}^3 \setminus \{R_1, \ldots, R_L\}$. It follows (from [25, 26] or the method in [15]) that $\{\varphi_i\}_{i=1,\ldots,M}$ and $\{\phi_{k,\ell}\}_{1 \leq k < \ell \leq M}$ are real analytic in $\mathbb{R}^3 \setminus \{R_1, \ldots, R_L\}$. This is the standard proof that solutions to the multiconfiguration equations (24)–(25) are real analytic away from the origin in $\mathbb{R}^3$ [20, 12].
Recall that \( R_1 = 0 \in \mathbb{R}^3 \). Note that (39)–(40), (37), and (35) imply that

\[
\gamma_i \left( -\Delta_y + 4|y|^2 V_K (\varphi_i)_K + \sum_{i,j,k,\ell=1}^{M} A_{ijk\ell} 4|y|^2 (\varphi_k,\ell)_K (\varphi_j)_K \right)
- \sum_{j=1}^{M} 4|y|^2 \lambda_{i,j} (\varphi_j)_K = 0, \quad 1 \leq i \leq M, \quad (41)
\]

\[
-\Delta_y (\varphi_{k,\ell})_K = 16\pi |y|^2 (\varphi_k)_K (\varphi_{\ell})_K, \quad 1 \leq k, \ell \leq M, \quad (42)
\]

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

Since the functions involved do not have the 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 below. This was carried out in [9, pp. 6–7] in a similar setting and details are therefore omitted here.

Since (using (35))

\[
4|y|^2 V_K (y) = -4Z_1 - \sum_{k=2}^{L} \frac{4Z_k |y|^2}{|K(y) - R_k|}
\]

is real analytic in a neighbourhood of 0 \( \in \mathbb{R}^3 \) (recall (35)), (41)–(42) shows that

\[
\{(\varphi_i)_K, (\varphi_{k,\ell})_K\}_{1\leq i,k,\ell\leq M} \quad (44)
\]

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

\[
\{(\varphi_i)_K\}_{1\leq i\leq M} \quad \text{and} \quad \{(\varphi_{k,\ell})_K\}_{1\leq k,\ell\leq M}
\]

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

\[
\varphi_K = \varphi \circ K : \mathcal{U} \to \mathbb{C}
\]

(46)

is real analytic.

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

\[
\varphi(x) = \varphi^{(1)}(x) + |x|\varphi^{(2)}(x) .
\]

(47)
Appendix A. 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:

$$\left(\Delta f\right)(K(y)) = \frac{1}{4|y|^2} \Delta f_K(y).$$

(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),

$$\int_{K^{-1}(U)} |\phi(K(y))|^2 \, dy = \frac{\pi}{4} \int_U \frac{|\phi(x)|^2}{|x|^2} \, dx.$$  \hfill (49)

In particular,

$$\|y|\phi_K\|^2_{L^2(K^{-1}(U))} = \frac{\pi}{4} \|\phi\|^2_{L^2(U)}. \hfill (50)$$

Remark A.2 ([9, Remark 3.2]). By a density argument, the isometry (50) allows to extend the composition by $K$ given by (36) (the pull-back $K^*$ by $K$) to a map

$$K^* : L^2(U, dx) \to L^2(K^{-1}(U), \frac{4}{\pi} |y|^2 dy)$$

$$\phi \mapsto \phi_K$$

in the case when $U = B_3(0, r), r \in (0, \infty]$. This makes $\phi_K$ 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 $r = \infty$),

$$\lim_{n \to \infty} \int_{K^{-1}(U)} g(y)(\phi_n)K(y) \, dy = \int_{K^{-1}(U)} g(y)\phi_K(y) \, dy.$$ \hfill (51)

This follows from Schwarz’ inequality and (50),

$$\left| \int_{K^{-1}(U)} g(y)((\phi_n)K(y) - \phi_K(y)) \, dy \right|$$

$$\leq \left( \int_{K^{-1}(U)} \frac{|g(y)|^2}{|y|^2} \, dy \right)^{1/2} \|y|((\phi_n)K - \phi_K)\|_{L^2(K^{-1}(U))}$$

$$= \frac{\sqrt{\pi}}{2} \left( \int_{K^{-1}(U)} \frac{|g(y)|^2}{|y|^2} \, dy \right)^{1/2} \|\phi_n - \phi\|_{L^2(U)} \to 0, \ n \to \infty.$$
Here the $y$-integral clearly converges since $g \in C^\infty(\mathbb{R}^4)$ ($g \in C_0^\infty(\mathbb{R}^4)$, if $r = \infty$).

Acknowledgement. This research was (partially) completed while TØS was visiting the Institute for Mathematical Sciences, National University of Singapore in 2008. SF is supported by the Danish Research Council, the Lundbeck Foundation and by the European Research Council under the European Community’s Seventh Framework Programme (FP7/2007-2013)/ERC grant agreement n° 202859. TØS is partially supported by The Danish Natural Science Research Council, under the grant ‘Mathematical Physics and Partial Differential Equations’.

References


(S. Fournais) Department of Mathematical Sciences, University of Aarhus, Ny Munkegade, Building 1530, DK-8000 Århus C, Denmark.
E-mail address: fournais@imf.au.dk

(S. Fournais on leave from) CNRS and Laboratoire de Mathématiques d’Orsay, Univ Paris-Sud, Orsay CEDEX, F-91405, France.

(M. Hoffmann-Ostenhof) Fakultät für Mathematik, Universität Wien, Nordbergstrasse 15, A-1090 Vienna, Austria.
E-mail address: maria.hoffmann-ostenhof@univie.ac.at

(T. Hoffmann-Ostenhof) Institut für Theoretische Chemie, Währingerstrasse 17, Universität Wien, A-1090 Vienna, Austria.

(T. Hoffmann-Ostenhof, 2nd address) The Erwin Schrödinger International Institute for Mathematical Physics, Boltzmanngasse 9, A-1090 Vienna, Austria.
E-mail address: thoffman@esi.ac.at

(T. Østergaard Sørensen) Department of Mathematical Sciences, Aalborg University, Fredrik Bajers Vej 7G, DK-9220 Aalborg East, Denmark.
E-mail address: sorensen@math.aau.dk