COMMENT ON ‘SOLUTIONS TO QUASI-RELATIVISTIC MULTI-CONFIGURATIVE HARTREE-FOCK EQUATIONS IN QUANTUM CHEMISTRY’, BY C. ARGAEZ & M. MELGAARD

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ABSTRACT. In a recent paper published in *Nonlinear Analysis: Theory, Methods & Applications*, C. Argaez and M. Melgaard studied excited states for pseudo-relativistic multi-configuration methods. Their paper follows a previous work of mine in the non-relativistic case (*Arch. Rat. Mech. Anal* 171, 2004). The main results of the paper of C. Argaez and M. Melgaard are correct, but the proofs are both wrong and incomplete.

In a recent paper [1] published in *Nonlinear Analysis: Theory, Methods & Applications*, C. Argaez and M. Melgaard studied the existence of excited states in a nonlinear model of quantum chemistry called multi-configuration. Their paper extends to the pseudo-relativistic setting some results which I have obtained in the non-relativistic case in [13]. The main results of the paper of C. Argaez and M. Melgaard are correct, but the proofs are both wrong and incomplete. The purpose of this letter is to explain why.

In the paper of Argaez-Melgaard, there is an important confusion between Hartree-Fock (HF) and multi-configuration (MC) theories. Indeed, sections 5, 7 and 8 in [1] have simply been copied and pasted from a previous paper [7] of Enstedt-Melgaard on pseudo-relativistic Hartree-Fock equations, without being of any help in the multi-configuration case.

Let me quickly re-explain the difference between the Hartree-Fock and multi-configuration models. The aim of these two nonlinear theories is to approximate the solutions of the many-body Schrödinger equation, describing electrons in atoms and molecules. The Hamiltonian of the system is the operator

\[ H_{NR/R}^\text{NR} := \sum_{j=1}^{N} \left( T_{x_j}^{NR/R} + V(x_j) \right) + \sum_{1 \leq k < \ell \leq N} \frac{1}{|x_k - x_\ell|} \]

acting on the subspace \( \bigwedge_1^N L^2(\mathbb{R}^3) \) of antisymmetric functions \( \Psi(x_1, ..., x_N) \) in \( L^2((\mathbb{R}^3)^N) \). The function \( V \) is the electrostatic potential induced by the nuclei in the system which, in the Born-Oppenheimer approximation, are treated as classical pointlike particles:

\[ V(x) := -\sum_{k=1}^{M} \frac{z_k}{|x - R_k|} \]

Here \( z_k > 0 \) and \( R_k \in \mathbb{R}^3 \) are, respectively, the charges and positions of the nuclei. The total nuclear charge is \( Z = \sum_{k=1}^{M} z_k \). The operator \( T_{x_j}^{NR/R} \) describes the kinetic
energy of the electrons. In non-relativistic quantum mechanics

\[ T^{\text{NR}} = -\frac{\Delta}{2}. \]

Relativistic particles should be described by the Dirac operator but there is no consistent theory for interacting systems at present. It is therefore useful to test some ideas on the so-called pseudo-relativistic operator

\[ T^R = \alpha^2 \left( \sqrt{1 - \alpha^2 \Delta} - 1 \right). \]

Here \( \alpha > 0 \) is the (bare) fine structure constant whose inverse is the speed of light. Pseudo-relativistic many-body systems based on \( T^R \) have been considered before in several important works including [15, 18-20, 23, 24]. The quadratic form associated with \( H^R \) is not always bounded from below (as opposed to the case of \( H^{\text{NR}} \)) but it is so when \( \alpha Z \leq 2/\pi \), by the Hardy-Kato inequality. In this case \( H^R \) is well defined by Friedrichs’ method and it has similar properties as in the non-relativistic case. In particular, when \( N < Z + 1 \) and \( \alpha Z < 2/\pi \), there are infinitely many eigenvalues \( \lambda_k \)'s below its essential spectrum [23, 24], corresponding to Schrödinger’s equation

\[ H^{\text{NR}/R} \Psi_k = \lambda_k \Psi_k. \]

For any normalized wave-function \( \Psi \), it is convenient to define the one-particle density matrix \( \gamma_{\Psi} \) by its integral kernel

\[ \gamma_{\Psi}(x, y) = N \int_{\mathbb{R}^3} dx_2 \cdots \int_{\mathbb{R}^3} dx_N \overline{\Psi(x, x_2, \ldots, x_N)} \Psi(y, x_2, \ldots, x_N). \]

This is a self-adjoint operator on \( L^2(\mathbb{R}^3) \) such that \( 0 \leq \gamma_{\Psi} \leq 1 \) and \( \text{Tr}(\gamma_{\Psi}) = N \). Any one-body observable can be expressed in terms of \( \gamma_{\Psi} \) only. For instance,

\[ \left\langle \Psi, \left( \sum_{j=1}^{N} \left( T^{\text{NR}/R}_{x_j} + V(x_j) \right) \right) \Psi \right\rangle_{L^2((\mathbb{R}^3)^N)} = \text{Tr}_{L^2(\mathbb{R}^3)} \left( T^{\text{NR}/R} + V \right) \gamma_{\Psi} \]

where both sides are interpreted in the sense of quadratic forms. On the other hand, the electronic Coulomb repulsion (the second sum in formula (1)) is a two-body operator which cannot be expressed in terms of \( \gamma_{\Psi} \) only, except for very specific states like Hartree-Fock states.

The Hartree-Fock method [17, 21] consists in restricting the many-body energy to wave-functions which are a single Slater determinant

\[ \Psi_{\text{HF}}(x_1, \ldots, x_N) = (\varphi_1 \wedge \cdots \wedge \varphi_N)(x_1, \ldots, x_N) := \frac{1}{\sqrt{N!}} \det(\varphi_i(x_j)), \]

where \( \langle \varphi_i, \varphi_j \rangle = \delta_{ij} \). Such states are completely described by their one-particle density matrix, which is the orthogonal projection on \( \text{span}(\varphi_1, \ldots, \varphi_N) \):

\[ \gamma_{\Psi_{\text{HF}}} = \sum_{j=1}^{N} |\varphi_j\rangle \langle \varphi_j|. \]

In particular, the two-body energy (hence also the total energy) can be expressed in terms of \( \gamma_{\Psi_{\text{HF}}} \) only. This fact is used in modern theoretical studies of HF-type models, as pioneered by Bach, Lieb, and Solovej [24, 16, 22], as well as in numerical optimization techniques [4].
The multi-configuration methods are based on the observation that Slater determinants span the whole many-body space. The many-body energy is then restricted to wave-functions which are a finite linear combination of Slater determinants:

\[ \Psi_{MC}(x_1, \ldots, x_N) = \sum_{1 \leq i_1 < \cdots < i_N \leq K} a_{i_1 \ldots i_N} \varphi_{i_1} \wedge \cdots \wedge \varphi_{i_N}. \]

The unknowns are the mixing coefficients \( a_{i_1 \ldots i_N} \) which must satisfy the normalization constraint \( \sum |a_{i_1 \ldots i_N}|^2 = 1 \) and the orbitals \( \varphi_1, \ldots, \varphi_K \) which must be orthonormal: \( \langle \varphi_i, \varphi_j \rangle = \delta_{ij} \). When \( K = N \) or when all the \( a_{i_1 \ldots i_N} \)'s vanish except one, we are back to the HF method. The MC energy is nothing but the many-body energy of such special states, expressed in terms of the mixing coefficients \( a_{i_1 \ldots i_N} \)'s and the orbitals \( \varphi_1, \ldots, \varphi_K \). In general, the interaction energy cannot be expressed only in terms of the one-body density matrix. The MC equations consist of a system of \( K \) coupled nonlinear PDE's for the \( \varphi_j \)'s, together with a \( \binom{K}{N} \)-dimensional eigenvalue equation for the \( a_{i_1 \ldots i_N} \)'s.

The existence of minimizers for non-relativistic MC was proved in a fundamental paper of Friesecke [9] and, later, in a paper of mine [13], with a different method based on previous works by Lions [21] and Fang-Ghoussoub [8, 11]. This technique allowed me to construct specific critical points of the MC energy, interpreted as approximate excited states in a certain sense. This is what was extended to the pseudo-relativistic case in the paper of Argaez-Melgaard.

Except for the sections copied from [7], the paper of Argaez-Melgaard follows very closely my paper [13]. I think it is fine to copy the literature, as long as the source is clearly mentioned, which is debatable here. The method of [13] works also in the pseudo-relativistic case, except for some minor steps. One difficulty is that the potential term involving \( V \) is not continuous for the \( H^{1/2}(\mathbb{R}^3) \) weak topology:

\[ \varphi_n \rightharpoonup \varphi \text{ weakly in } H^{1/2}(\mathbb{R}^3) \iff \int_{\mathbb{R}^3} |\varphi_n(x)|^2 \frac{dx}{|x|} \to \int_{\mathbb{R}^3} |\varphi(x)|^2 \frac{dx}{|x|} \]

Said differently, the operator \((1 - \Delta)^{-1/4}|x|^{-1}(1 - \Delta)^{-1/4}\) is not compact. The result corresponding to \([8] \) is true in the non-relativistic case in which \( H^{1/2}(\mathbb{R}^3) \) is replaced by \( H^1(\mathbb{R}^3) \), and this was used in [13] as well as in most papers dealing with non-relativistic atomic models. What is true in the pseudo-relativistic case, however, is that the total one-body energy is weakly lower semi-continuous, that is

\[ \varphi_n \rightharpoonup \varphi \text{ weakly in } H^{1/2}(\mathbb{R}^3) \implies \liminf_{n \to \infty} \langle \varphi_n, (T^R + V)\varphi_n \rangle \geq \langle \varphi, (T^R + V)\varphi \rangle \]

as soon as \( \alpha Z < 2/\pi \). This well-known fact was already employed in pseudo-relativistic Hartree-Fock theory by Dall’Acqua, Østergaard Sørensen and Stockmeyer in [5]. The reason why \([7] \) is true is that \( T^R + V \) can be written as \( T^R + V = (T^R + V)^+ - (T^R + V)_- \) where \((T^R + V)^+ \geq 0 \) and \((T^R + V)_- \) is compact \([8] \). It is indeed a general fact that the quadratic form of a bounded-below operator \( A \) is weakly lower semi-continuous for the associated topology, if and only if the essential spectrum of \( A \) does not go below \( 0 \). One can verify that \([7] \) is sufficient to adapt the proof of [13] to the pseudo-relativistic case.

\[ ^1 \text{In [6] it was even shown, using ideas of [3], that } (T^R + V)_- \text{ is Hilbert-Schmidt, but this is not necessary here.} \]
In the paper of Argaez-Melgaard, the property (7) is somewhat proved in the appendix. It is formulated in terms of density matrices, which is fine but not necessary. Even though the same result in the Enstedt-Melgaard paper [7, p. 14] simply referred to [6], it is detailed again in the Argaez-Melgaard paper, without even mentioning [6].

What is however completely wrong in the Argaez-Melgaard paper is the treatment of the two-body repulsion between the electrons. This term is non-negative and the proof of [13] applies without any difficulty. Instead, Argaez and Melgaard “switch to the density operator formulation” on page 396, and they associate to any MC wave-function Ψ of the form (5) the ‘density’ operator

\[
\mathcal{D} = \sum_{1 \leq i_1 < \cdots < i_N \leq K} a_{i_1 \ldots i_N} \left( |\varphi_{i_1}\rangle \langle \varphi_{i_1}| + \cdots + |\varphi_{i_N}\rangle \langle \varphi_{i_N}| \right).
\]

Then, on pages 396-397 and in the appendix, they use that the MC total energy is equal to the HF energy of \( \mathcal{D} \). This is obviously wrong (the energy is quadratic in the \( a_{i_1 \ldots i_N} \) but the one-body term in the HF energy is linear). The operator \( \mathcal{D} \) is not even related to the true density matrix \( \gamma_{\Psi} \) (except when all the \( a_{i_1 \ldots i_N} \) vanish but for one, which equals 1).

Even if we forget for a moment that the energy cannot be expressed in terms of \( \mathcal{D} \), most of the mathematical arguments of Argaez-Melgaard based on \( \mathcal{D} \) are incorrect. The main difficulty that \( \mathcal{D} \) is not a non-negative operator (the \( a_{i_1 \ldots i_N} \) can be negative), is avoided in a very questionable fashion. In several places, the authors seem to forget that the \( a_{i_1 \ldots i_N} \)'s have no sign and, when necessary, they suddenly replace \( a_{i_1 \ldots i_N} \) by the absolute value \( |a_{i_1 \ldots i_N}| \) (see, e.g., the liminf argument at the bottom of page 402). Even the nonlinear HF interaction term is not weakly lower semi-continuous when the density matrix has no sign, and (A.14) is not correct.

Let me end this Letter by mentioning another issue with the paper of Argaez and Melgaard. Their main result (Proposition 9.1) contains the statement that the limit of a Palais-Smale sequences for the MC energy always has a rank equal to \( K - 1 \) or \( K \). The non-relativistic equivalent to this statement was proved independently in [10, 14], based on a previous method of Le Bris [12]. It relies on the fact that the orbitals \( \varphi_i \)'s of a solution to the MC equations are real-analytic away from the nuclear positions. This fact is not proved by Argaez and Melgaard, who instead refer to ‘a future work’ on page 397. So the corresponding statement 5 in Proposition 9.1 is in fact not proved in the paper. Fortunately, the real-analyticity was recently proved by Dall’Acqua, Fournais, Østergaard Sørensen and Stockmeyer in [5], and Proposition 9.1 is finally correct.

As a conclusion, the paper of Argaez and Melgaard refers improperly to the literature and some parts of the proofs are wrong.

**References**

[1] C. Argaez and M. Melgaard, Solutions to quasi-relativistic multi-configurative Hartree-Fock equations in quantum chemistry, Nonlinear Analysis: Theory, Methods & Applications, 75 (2012), pp. 384–404.

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\[\text{[2]}\text{The proof of this in the Hartree-Fock case was made available on arXiv in the first version of [5], before the submission of the paper of Argaez-Melgaard. The observation that the proof works the same in the MC case was added in the second version of [5], after the publication of [1].}\]
Comment on a paper by C. Argaez & M. Melgaard

[2] V. Bach, Error bound for the Hartree-Fock energy of atoms and molecules, Commun. Math. Phys., 147 (1992), pp. 527–548.

[3] J. M. Barbaroux, W. Farkas, B. Helffer, and H. Siedentop, On the Hartree-Fock equations of the electron-postron field, Commun. Math. Phys., 255 (2005), pp. 131–159.

[4] É. Cancès, M. Defranceschi, W. Kutzelnigg, C. Le Bris, and Y. Maday, Computational quantum chemistry: a primer, in Handbook of numerical analysis, Vol. X, Handb. Numer. Anal., X, North-Holland, Amsterdam, 2003, pp. 3–270.

[5] A. Dall’Acqua, S. Fournais, T. Østergaard Sørensen, and E. Stockmeyer, Real analyticity away from the nucleus of pseudorelativistic Hartree-Fock orbitals, Analysis & PDE, to appear (2011).

[6] A. Dall’Acqua, T. Østergaard Sørensen, and E. Stockmeyer, Hartree-Fock theory for pseudorelativistic atoms, Annal. Henri Poincaré, 9 (2008), pp. 711–742.

[7] M. Enstedt and M. Melgaard, Existence of infinitely many distinct solutions to the quasirelativistic Hartree-Fock equations, Int. J. Math. Math. Sci., (2009), p. 651871.

[8] G. Fang and N. Ghoussoub, Morse-type information on Palais-Smale sequences obtained by min-max principles, Comm. Pure Appl. Math., 47 (1994), pp. 1595–1653.

[9] G. Friesecke, The multiconfiguration equations for atoms and molecules: charge quantization and existence of solutions, Arch. Ration. Mech. Anal., 169 (2003), pp. 35–71.

[10] ———, On the infinitude of non-zero eigenvalues of the single-electron density matrix for atoms and molecules, R. Soc. Lond. Proc. Ser. A Math. Phys. Eng. Sci., 459 (2003), pp. 47–52.

[11] N. Ghoussoub, Duality and perturbation methods in critical point theory, vol. 107 of Cambridge Tracts in Mathematics, Cambridge University Press, Cambridge, 1993. With appendices by David Robinson.

[12] C. Le Bris, A general approach for multiconfiguration methods in quantum molecular chemistry, Ann. Inst. Henri Poincaré Anal. Non Linéaire, 11 (1994), pp. 441–484.

[13] M. Lewin, Solutions of the multiconfiguration equations in quantum chemistry, Arch. Ration. Mech. Anal., 171 (2004), pp. 83–114.

[14] ———, Some nonlinear models in Quantum Mechanics, PhD thesis, University of Paris-Dauphine, June 2004.

[15] R. T. Lewis, H. Siedentop, and S. Vugalter, The essential spectrum of relativistic multi-particle operators, Ann. Inst. Henri Poincaré, 67 (1997), pp. 1–28.

[16] E. H. Lieb, Variational principle for many-fermion systems, Phys. Rev. Lett., 46 (1981), pp. 457–459.

[17] E. H. Lieb and B. Simon, The Hartree-Fock theory for Coulomb systems, Commun. Math. Phys., 53 (1977), pp. 185–194.

[18] E. H. Lieb and W. E. Thirring, Gravitational collapse in quantum mechanics with relativistic kinetic energy, Ann. Physics, 155 (1984), pp. 494–512.

[19] E. H. Lieb and H.-T. Yau, The Chandrasekhar theory of stellar collapse as the limit of quantum mechanics, Commun. Math. Phys., 112 (1987), pp. 147–174.

[20] ———, The stability and instability of relativistic matter, Commun. Math. Phys., 118 (1988), pp. 177–213.

[21] P.-L. Lions, Solutions of Hartree-Fock equations for Coulomb systems, Commun. Math. Phys., 109 (1987), pp. 33–97.

[22] J. P. Solovej, Proof of the ionization conjecture in a reduced Hartree-Fock model., Invent. Math., 104 (1991), pp. 291–311.

[23] G. M. Zhislin, The spectrum of Hamiltonians of pseudorelativistic electrons of molecules in spaces of functions with permutational and point symmetry, Funktsional. Anal. i Prilozhen., 40 (2006), pp. 65–69.

[24] G. M. Zhislin and S. A. Vugalter, On the discrete spectrum of Hamiltonians for pseudorelativistic electrons, Izv. Ross. Akad. Nauk Ser. Mat., 66 (2002), pp. 71–102.

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