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Adel Almoukhalalati, Stefan Knecht, Hans Jørgen Aagaard Jensen, Kenneth G. Dyall, Trond Saue. Electron correlation within the relativistic no-pair approximation. *Journal of Chemical Physics*, 2016, 145 (7), pp.074104. 10.1063/1.4959452 . hal-01381814

HAL Id: hal-01381814

<https://hal.science/hal-01381814>

Submitted on 21 Jan 2020

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Citation: *The Journal of Chemical Physics* **145**, 074104 (2016); doi: 10.1063/1.4959452

View online: <http://dx.doi.org/10.1063/1.4959452>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/145/7?ver=pdfcov>

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Electron correlation within the relativistic no-pair approximation

Adel Almoukhalalati,¹ Stefan Knecht,² Hans Jørgen Aa. Jensen,³ Kenneth G. Dyall,⁴ and Trond Saue^{1,a)}

¹Laboratoire de Chimie et Physique Quantique, UMR 5626 CNRS — Université Toulouse III-Paul Sabatier, 118 route de Narbonne, F-31062 Toulouse, France

²ETH Zürich, Laboratorium für Physikalische Chemie, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

³Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark

⁴Dirac Solutions, 10527 NW Lost Park Drive, Portland, Oregon 97229, USA

(Received 11 May 2016; accepted 12 July 2016; published online 16 August 2016)

This paper addresses the definition of correlation energy within 4-component relativistic atomic and molecular calculations. In the nonrelativistic domain the correlation energy is defined as the difference between the exact eigenvalue of the electronic Hamiltonian and the Hartree-Fock energy. In practice, what is reported is the basis set correlation energy, where the “exact” value is provided by a full Configuration Interaction (CI) calculation with some specified one-particle basis. The extension of this definition to the relativistic domain is not straightforward since the corresponding electronic Hamiltonian, the Dirac-Coulomb Hamiltonian, has no bound solutions. Present-day relativistic calculations are carried out within the no-pair approximation, where the Dirac-Coulomb Hamiltonian is embedded by projectors eliminating the troublesome negative-energy solutions. Hartree-Fock calculations are carried out with the implicit use of such projectors and only positive-energy orbitals are retained at the correlated level, meaning that the Hartree-Fock projectors are frozen at the correlated level. We argue that the projection operators should be optimized also at the correlated level and that this is possible by full Multiconfigurational Self-Consistent Field (MCSCF) calculations, that is, MCSCF calculations using a no-pair full CI expansion, but including orbital relaxation from the negative-energy orbitals. We show by variational perturbation theory that the MCSCF correlation energy is a pure MP2-like correlation expression, whereas the corresponding CI correlation energy contains an additional relaxation term. We explore numerically our theoretical analysis by carrying out variational and perturbative calculations on the two-electron rare gas atoms with specially tailored basis sets. In particular, we show that the correlation energy obtained by the suggested MCSCF procedure is smaller than the no-pair full CI correlation energy, in accordance with the underlying minmax principle and our theoretical analysis. We also show that the relativistic correlation energy, obtained from no-pair full MCSCF calculations, scales at worst as X^{-2} with respect to the cardinal number X of our correlation-consistent basis sets optimized for the two-electron atoms. This is better than the X^{-1} scaling suggested by previous studies, but worse than the X^{-3} scaling observed in the nonrelativistic domain. The well-known $1/Z$ -expansion in nonrelativistic atomic theory follows from coordinate scaling. We point out that coordinate scaling for consistency should be accompanied by velocity scaling. In the nonrelativistic domain this comes about automatically, whereas in the relativistic domain an explicit scaling of the speed of light is required. This in turn explains why the relativistic correlation energy to the lowest order is not independent of nuclear charge, in contrast to nonrelativistic theory. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4959452>]

I. INTRODUCTION

Electron correlation remains a central challenge of molecular quantum mechanics, as well as many other domains of physics and chemistry. In 1958 Löwdin proposed the following definition of the associated correlation energy: “The correlation energy for a certain state with respect to a specified Hamiltonian is the difference between the exact eigenvalue of the Hamiltonian and its expectation value in the Hartree-Fock approximation for the state under consideration.”¹ Löwdin

carefully stressed that the exact energy so defined is not equal to the experimental energy since it misses rovibrational contributions and relativistic effects (as well as QED effects, one may add). The present-day operational definition of the nonrelativistic correlation energy is the energy difference between a full Configuration Interaction (CI) and a Hartree-Fock (HF) calculation in some specified 1-particle basis and is more precisely denoted the basis set correlation energy.²

In the relativistic domain the situation is more problematic: when the nonrelativistic one-electron Hamiltonian is replaced by the 4-component Dirac Hamiltonian the resulting Dirac-Coulomb (DC) Hamiltonian has no bound solutions. This unpleasant situation, first pointed out by Brown and

^{a)}Electronic mail: trond.sau@irsamc.ups-tlse.fr; <http://dirac.ups-tlse.fr/sau>

Ravenhall,³ is due to the presence of negative-energy solutions of the Dirac Hamiltonian, which for the many-electron problem means that a chosen reference determinant of bound electronic solutions is degenerate with an infinite number of determinants containing continuum solutions of both positive and negative energy. Brown and Ravenhall suggested to block continuum dissolution by embedding the relativistic electronic Hamiltonian in operators projecting out the negative-energy solutions of the one-electron problem, leading to the so-called “no-pair” Hamiltonian.⁴ Brown and Ravenhall furthermore proposed to use projection operators defined with respect to the free-particle Dirac Hamiltonian. Theoretical analysis shows, though, that this may introduce negative-energy solutions into the Hamiltonian rather than remove them,⁵ which can also be shown numerically.⁶ Mittleman proposed instead to optimize the projection operators according to the problem at hand and demonstrated that the appropriate projection operators for Hartree-Fock calculations are defined with respect to the 4-component relativistic Fock operator of the problem.⁷ This is the approach taken by most modern-day 4-component relativistic molecular calculations: the SCF algorithm of Hartree-Fock (and Kohn-Sham) is based on the implicit use of projectors in that the selection of orbitals for the construction of the mean-field potential in each iteration is not based on an Aufbau principle as in the nonrelativistic domain, rather on the identification of the lowest bound orbitals in the energy gap separating the negative- and positive-energy continua (or rather the discrete representation in a finite basis approximation). This in turn hinges on proper construction of the 1-particle basis using the kinetic balance prescription.^{8,9} At the correlated level the no-pair approximation is imposed by using only positive-energy orbitals from the preceding HF calculation for the construction of the N -particle basis.

It should be mentioned that there have been reports in the literature of 4-component relativistic CI calculations using Slater determinants containing both positive- and negative-energy orbitals, and where it was possible to identify bound solutions amongst the sea of continuum solutions.^{10–14} Pestka *et al.* treat such solutions as resonances and extract them by complex-coordinate rotation techniques.¹⁵ However, these approaches imply that matter is not stable and are therefore fundamentally not satisfactory. Another approach is to go to full-fledged QED, which recently has attracted considerable attention in the molecular domain.^{16–24} In the present contribution, however, we seek a relativistic definition of the electron correlation energy within the current paradigm of relativistic molecular calculations, which is the no-pair approximation and which implies that the negative-energy orbitals are treated as an orthogonal complement. It is true that even within the present paradigm negative-energy orbitals come into play. For instance, in perturbative calculations of magnetic properties, the diamagnetic contribution is recovered from the negative-energy orbitals of the unperturbed problem.^{25–27} However, in such calculations the negative-energy orbitals simply constitute a basis for the construction of perturbative corrections to the wave function, whereas in QED they take on physical reality.

We argue that a full CI within the Hartree-Fock no-pair approximation according to the proposal by Mittleman⁷

does *not* constitute an “exact” calculation for the evaluation of the relativistic correlation energy since the projection operators are not fully optimized, but remain frozen at the HF level. This model is designated HF-CI in the following. Saue and Visscher in 2003 therefore proposed that the proper reference for molecular correlated calculations is a no-pair Multiconfigurational SCF (MCSCF) calculation, that is, a calculation in which the CI expansion is limited to positive-energy orbitals only, but in which orbital rotations between positive- and negative-energy solutions are allowed, thus allowing full orbital (and projector) optimization.¹⁶ In the present contribution we provide further arguments for this view using variational perturbation theory and present no-pair full HF-CI and MCSCF calculations of the helium-like rare gases.

The helium isoelectronic series has been a test bench for electron correlation methods since the beginning of quantum theory. The 1913 Bohr model of the atom²⁸ marks a milestone in modern physics, providing a rationale for the Rydberg formula for hydrogen. Yet, when Bohr in the same year applied his model to the helium atom,²⁹ the result was less encouraging, overshooting the experimental ionization energy (24.587 387 eV) by more than 4 eV. It took more than ten years of concentrated efforts and the development of the “new quantum theory” to reach acceptable results.^{30–34} The contributions of Hylleraas deserve particular mention.^{35,36} His 1928 variational calculation gave a helium ground state energy of $-2.895 E_h$.³³ The year after he reported an improved value of $-2.9037 E_h$,³⁷ where the five digits agree with the five first digits of the nonrelativistic energy calculated to over 40 digit accuracy by Nakashima and Nakatsuji in 2007.³⁸ Hylleraas achieved this by explicit inclusion of the interelectronic coordinate r_{12} in his trial function, thus providing a precursor to modern-day explicitly correlated methods.^{39–41} Hylleraas also introduced the expansion of the ground state energy of the helium isoelectronic series in terms of inverse nuclear charge Z ⁴²

$$E^{exact} = -Z^2 + \frac{5}{8}Z - 0.15767 + O(Z^{-1}) \quad (1)$$

(reported in E_h). A corresponding $1/Z$ expansion of the HF energy was later reported by Linderberg⁴³

$$E^{HF} = -Z^2 + \frac{5}{8}Z - 0.11100 + O(Z^{-1}), \quad (2)$$

showing that the nonrelativistic correlation energy to the lowest order is independent of nuclear charge

$$E_{corr} = E^{exact} - E^{HF} = -0.04667 + O(Z^{-1}). \quad (3)$$

This fascinating result has been used to construct new models of electron correlation.^{44,45} However, it is not valid in the relativistic domain, as shown by no-pair full CI calculations by Watanabe and Tatewaki.⁴⁶

In the present contribution we report no-pair full HF-CI and full MCSCF calculations of the helium-like rare gas atoms He, Ne⁺⁸, Ar⁺¹⁶, Kr⁺³⁴, Xe⁺⁵², Rn⁺⁸⁴, and Uuo⁺¹¹⁶ using a sequence of specially tailored correlation-consistent Gaussian basis sets energy-optimized for the $1s^2$ ground states.⁴⁷ Our paper is organized as follows: in Section II we derive perturbation expressions for the

correlation energy in the nonrelativistic and relativistic domain. In Section III we provide computational details, in particular about the generation of the specially tailored basis sets employed in this study. In Section IV we present and discuss our results and then conclude in Section V. Throughout this work we employ SI-based atomic units,⁴⁸ but retain electron mass m and fundamental charge e for clarity.

II. THEORY

A. Variational perturbation theory

In this section we shall derive expressions for the electron correlation energy of nonrelativistic and relativistic two-electron atoms. Our tool will be variational perturbation theory as defined by Helgaker and Jørgensen,⁴⁹ in contrast to other meanings,⁵⁰ including the variational-perturbation procedure developed by Hylleraas (the Hylleraas functional).^{51,52} The key feature of this approach is to assume that the expectation value E of the Hamiltonian

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1,$$

with respect to some suitable trial function $|\tilde{0}\rangle \equiv |\tilde{0}(\tilde{\zeta})\rangle$ with variational parameters gathered in the vector $\tilde{\zeta}$, has been optimized

$$\left. \frac{\partial E}{\partial \zeta_i} \right|_{\lambda} = 0 \quad (4)$$

for any value of the perturbation strength λ . The optimized variational parameters then become functions of the perturbation strength λ , that is, $\boldsymbol{\zeta} \equiv \boldsymbol{\zeta}(\lambda)$ and can be calculated to any order starting from the variational condition (4). This in turn allows us to calculate the perturbation expansion

$$E(\lambda) = E_0 + \left. \frac{dE}{d\lambda} \right|_{\lambda=0} \lambda + \frac{1}{2} \left. \frac{d^2E}{d\lambda^2} \right|_{\lambda=0} \lambda^2 + \dots$$

We shall consider three variational methods. We employ exponential parametrizations, which simplifies mathematical manipulations since (i) redundant parameters (parameters that do not change the energy) are easily identified and eliminated⁵³ and (ii) no constraints (such as orthonormality of orbitals) need to be introduced in terms of Lagrange multipliers. We express the Hartree-Fock trial function as

$$|HF\rangle = \exp[-\hat{\kappa}] |0\rangle, \quad \hat{\kappa} = \sum_{p>q} (\kappa_{pq} \hat{p}^\dagger \hat{q} - \kappa_{pq}^* \hat{q}^\dagger \hat{p}),$$

where $\hat{\kappa}$ is the orbital rotation operator⁵⁴⁻⁵⁶ and $|0\rangle$ the reference determinant, corresponding to the variational solution of the zeroth-order Hamiltonian \hat{H}_0 . The CI trial function, on the other hand, is parametrized in terms of the state transfer operator⁵⁷ \hat{S}

$$|CI\rangle = \exp[-\hat{S}] |0\rangle, \quad (5)$$

$$\hat{S} = \sum_{M \in \{|M\rangle\} / \{|0\rangle\}} (s_M |M\rangle \langle 0| - s_M^* |0\rangle \langle M|),$$

where the summation runs over the elements of the orthonormal N -particle (determinant) basis $\{|M\rangle\}$ excluding the reference determinant $|0\rangle$. The HF and CI methods may be

considered special cases of MCSCF, as is clearly seen when the MCSCF trial function is expressed as

$$|MC\rangle = \exp[-\hat{\kappa}] \exp[-\hat{S}] |0\rangle.$$

In Sec. II B we consider the nonrelativistic case which leads to the partitioning of the electronic Hamiltonian chosen by Hylleraas for two-electron atoms and which we afterwards will extend to the relativistic domain. Further details are given in the Appendix.

B. Nonrelativistic case

The nonrelativistic wave equation for two electrons in the electrostatic field of a nucleus of charge Z and infinite mass reads

$$\hat{H}\Psi(1,2) = E\Psi(1,2), \quad \hat{H} = \hat{h}_Z(1) + \hat{h}_Z(2) + V_{ee},$$

where the two-electron interaction is the instantaneous Coulomb interaction

$$V_{ee} = \frac{e^2}{r_{12}}.$$

The one-electron Hamiltonian is given by

$$h_Z(i) = \frac{p_i^2}{2m} + V_{eN}(i), \quad V_{eN} = -e\phi_{nuc},$$

$$\phi_{nuc}(\mathbf{r}_1) = Ze \int \frac{\rho_{nuc}(\mathbf{r}_2)}{r_{12}} d^3\mathbf{r}_2,$$

where the nuclear charge distribution ρ_{nuc} is normalized to unity. In the nonrelativistic domain the nucleus is usually modeled as a point charge such that

$$V_{eN} = -Ze^2 \int \frac{\delta(\mathbf{r}_2)}{r_{12}} d^3\mathbf{r}_2 = -\frac{Ze^2}{r},$$

when the nucleus is placed at the origin.

Rather than focusing exclusively on the helium atom, Hylleraas generalized his study to two-electron atoms of arbitrary nuclear charge Z ,⁴² apparently spurred by the accurate measurements of the ionization energies of Li^+ and Be^{2+} by Ericson and Edlén.⁵⁸ He observed^{55,51} that the one-electron problem

$$\left[-\frac{1}{2m} \nabla^2 - \frac{Ze^2}{r} \right] \varphi_Z(\mathbf{r}) = \varepsilon_Z \varphi_Z(\mathbf{r}) \quad (6)$$

could be expressed as

$$\left[-\frac{1}{2m} \nabla^2 - \frac{e^2}{r} \right] \varphi_{Z=1}(\mathbf{r}) = \varepsilon_{Z=1} \varphi_{Z=1}(\mathbf{r}), \quad \varepsilon_Z = Z^2 \varepsilon_{Z=1},$$

upon coordinate scaling

$$\mathbf{r} \rightarrow Z^{-1}\mathbf{r}. \quad (7)$$

The underlying physics is perhaps not entirely clear, but it may be noted that spherical wave solutions to the corresponding free-particle problem are given by

$$\varphi_0(\mathbf{r}) = R_l(r, k) Y_{lm}(\theta, \phi), \quad R_l(r, k) = \sqrt{\frac{2}{\pi}} k j_l(kr),$$

$$k^2 = 2mE,$$

where the radial functions are given in terms of spherical Bessel functions of the first kind with the *scaled* coordinate kr as argument.

Upon application of the same coordinate scaling (7) to the two-electron problem one obtains

$$\left[\hat{h}_{Z=1}(1) + \hat{h}_{Z=1}(2) + \frac{1}{Z} V_{ee} \right] \Psi(1,2) = E' \Psi(1,2),$$

$$E = Z^2 E',$$

where the two-electron interaction appears as a perturbation with Z^{-1} as the corresponding perturbation parameter, leading to the well-known $1/Z$ expansion. In particular, one notes that in the limit of infinite nuclear charge the two-electron interaction vanishes, which does make physical sense.

Following Hylleraas, we partition the Hamiltonian as

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \quad \hat{H}_0 = \hat{h}_Z(1) + \hat{h}_Z(2), \quad \hat{H}_1 = \frac{e^2}{r_{12}}.$$

The zeroth-order wave function, for all three methods cited above, is a Slater determinant of orbitals of the *one-electron problem* (6)

$$\Phi_0 = |\varphi_{1s}^{(0)} \alpha \varphi_{1s}^{(0)} \beta|$$

and is the *exact* solution of the zeroth-order Hamiltonian \hat{H}_0 . In the [Appendix](#) we derive a perturbation expansion of the HF energy using variational perturbation theory

$$E^{HF} = \langle 0 | \hat{H}_0 | 0 \rangle + \langle 0 | \hat{H}_1 | 0 \rangle + E_2^{HF} + O(Z^{-1}),$$

$$E_2^{HF} = \sum_{ai} \frac{|F_{ia}^{(2)}|^2}{\varepsilon_i - \varepsilon_a}, \quad (8)$$

where the second-order contribution E_2^{HF} is expressed in terms of the occupied-virtual block of two-electron Fock matrix $F_{pq}^{(2)}$ using the orbitals of the one-electron problem. Here and in the following indices i, j, k, l, \dots refer to occupied orbitals, indices a, b, c, d, \dots refer to virtual orbitals, and indices p, q, r, s, \dots refer to general orbitals. Eq. (8) corresponds exactly to the expression (2) given by Linderberg.⁴³ One may note the relations $F_{ai}^{(2)} = F_{ai} \neq 0$, which is due to the use of the orbitals of the one-electron problem, rather than the optimized HF orbitals. From the denominator, the second-order contribution E_2^{HF} is negative, in accordance with the underlying minimization principle in the nonrelativistic domain.

In the [Appendix](#) we also show that the corresponding perturbation expansion of the HF-CI energy is

$$E^{CI} = \langle 0 | \hat{H}_0 | 0 \rangle + \langle 0 | \hat{H}_1 | 0 \rangle + E_2^{CI} + O(Z^{-1}),$$

$$E_2^{CI} = E_2^{HF} - \frac{1}{4} \sum_{ij} \sum_{ab} \frac{| \langle ij || ab \rangle |^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}. \quad (9)$$

The zeroth- and first-order terms are identical in the HF and CI expansions and cancel out when calculating the correlation energy. We also note that the second-order contribution consists of two terms, of which the first is identical to the second-order HF contribution and associated with relaxation. Only the second term contributes to the correlation energy

$$E_{corr} = E_2^{CI} - E_2^{HF} + O(Z^{-1})$$

$$= \sum_{ia} \frac{\langle ij || ab \rangle \langle ab || ij \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + O(Z^{-1}).$$

To the lowest order the correlation energy is thereby given by the second-order Møller-Plesset energy evaluated using the orbitals of the *one-electron* problem. It should be noted that due to the scaling properties shown above the energy contribution to any given order for an atom of charge Z_2 can be obtained by calculating the same contribution for a reference atom of charge Z_1 and then scaling this contribution by (Z_2/Z_1) of appropriate order.

C. Relativistic case

Let us next consider the relativistic two-electron atom. We start from a Hamiltonian of the form

$$\hat{H} = \hat{h}_D(1) + \hat{h}_D(2) + V_{ee}, \quad (10)$$

where the one-electron part is now given by the Dirac Hamiltonian

$$\hat{h}_D = \beta mc^2 + c(\boldsymbol{\alpha} \cdot \mathbf{p}) + V_{eN},$$

where c is the speed of light and β and $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ are the 4×4 Dirac matrices. The fully relativistic two-electron interaction involves the complete history of the electrons and will in the present work be approximated by the instantaneous Coulomb interaction

$$V_{ee} = \frac{e^2}{r_{12}} + O(c^{-2}) \approx \frac{e^2}{r_{12}}.$$

This truncated form defines the Dirac-Coulomb Hamiltonian,⁶ upon which most present-day 4-component relativistic molecular calculations are based.

We first consider the one-electron problem

$$\left[\beta mc^2 + c(\boldsymbol{\alpha} \cdot \mathbf{p}) - \frac{Ze^2}{r} \right] \varphi_Z = \varepsilon_Z \varphi_Z, \quad (11)$$

using a point charge model for the nucleus.

In his seminal 1928 paper on the relativistic wave equation for the electron,⁵⁹ Dirac derived the radial equation for hydrogenic systems, but did not provide an exact solution. This was done independently by Gordon⁶⁰ and Darwin.⁶¹ Remarkable are also the elegant solution provided by Pidduck⁶² in 1929 and the unified nonrelativistic and relativistic approach of Swainson and Drake.⁶³ Interestingly, Hylleraas also considered the relativistic hydrogen atom.⁶⁴ A recent historical account is provided by Mawhin and Ronveaux.⁶⁵

The energy spectrum of the relativistic hydrogen-like atom is sketched in Figure 1. We have aligned the relativistic energy scale with the nonrelativistic one by setting $E \rightarrow E' = E - mc^2$. This is formally done by the substitution $\beta \rightarrow \beta' = \beta - mc^2$ in Eq. (11). The spectrum shows bound solutions appearing in the forbidden $2mc^2$ energy gap of the relativistic free-particle problem. We may try to connect solutions of systems with different nuclear charge by coordinate scaling (7), as in the nonrelativistic case. However, this leads to the result

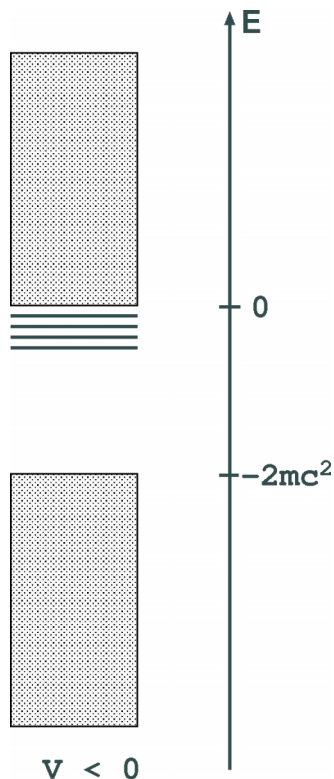


FIG. 1. Energy spectrum of a relativistic hydrogen atom. The energy has been shifted by mc^2 in order to align with the nonrelativistic energy scale.

$$\left[\beta mc^2 + Zc(\boldsymbol{\alpha} \cdot \mathbf{p}) - \frac{Z^2 e^2}{r} \right] \varphi_Z = \varepsilon_Z \varphi_Z,$$

from which it is not possible to factor out the nuclear charge. On the other hand, one may note that scaling (7) of position implies scaling of velocity, since the latter is the time derivative of the former. In the nonrelativistic case the velocity operator is \mathbf{p}/m and scaling is achieved automatically. In the relativistic case the velocity operator is $c\boldsymbol{\alpha}$, and one realizes that the coordinate scaling (7) has to be accompanied by velocity scaling $c \rightarrow Z^{-1}c$

$$Z^2 \left[\beta m(c/Z)^2 + (c/Z)(\boldsymbol{\alpha} \cdot \mathbf{p}) - \frac{e^2}{r} \right] \varphi_Z = \varepsilon_Z \varphi_Z.$$

Pursuing this approach the inverse nuclear charge will appear in front of the interaction term V_{ee} of the two-electron Hamiltonian (10), but the limit $Z \rightarrow \infty$ cannot be attained, since the energy gap $2mc^2$, in which the bound solutions live (cf. Figure 1), closes at $Z \sim 137$ and the Dirac equation effectively breaks down. It is still possible to connect energy contributions for an atom of charge Z_2 to those of a reference atom of Z_1 , but the reference calculation then has to be carried out at the appropriate scaled speed of light.

For relativistic atoms the $1/Z$ -expansion has been generalized to a double perturbation expansion in $1/Z$ and $Z^2\alpha^2$,^{66,67} where α is the fine-structure constant. We shall, however, retain the same partitioning of the electronic Hamiltonian as in the nonrelativistic case, the one-electron part now given by the Dirac Hamiltonian. The HF perturbation expansion is the same as in the nonrelativistic case (8), but it will be useful to distinguish between orbital rotations κ_{ai}^{++}

between positive-energy occupied (i) and virtual (a) orbitals and orbital rotations κ_{ai}^{-+} between the positive-energy occupied orbitals and negative-energy virtual orbitals. We therefore write the second-order HF energy contribution as

$$E_{2:rel}^{HF} = \sum_{a+i^+} \frac{|F_{i^+a^+}^{(2)}|^2}{\varepsilon_i^+ - \varepsilon_a^+} + \sum_{a-i^+} \frac{|F_{i^+a^-}^{(2)}|^2}{\varepsilon_i^+ - \varepsilon_a^-}, \quad (12)$$

where the first and second terms are associated with κ_{ai}^{++} and κ_{ai}^{-+} , respectively. Without further modifications of the Dirac-Coulomb Hamiltonian (10) the CI perturbation expansion is the same as in the nonrelativistic case (9), but now problematic, as pointed out by Brown and Ravenhall:³ an infinite number of doubly excited Slater determinants $|0_{ij}^{ab}\rangle$, with one virtual orbital from the positive-energy continuum and the other from the negative-energy one, are degenerate with the reference determinant $|0\rangle$ and so the Dirac-Coulomb Hamiltonian has no bound solutions. In order to cure what later became known as the Brown-Ravenhall disease, Brown and Ravenhall proposed to embed the Dirac-Coulomb Hamiltonian by projection operators eliminating the troublesome negative-energy orbitals. There are several possible choices of projectors: (i) one might use the projector Λ_+^{free} based on the free-particle solutions of the Dirac Hamiltonian, or (ii) the projector Λ_+^{bare} based on the bare-nucleus solutions of the Dirac Hamiltonian, that is, the one-electron part of the Dirac-Coulomb Hamiltonian, or (iii) the projector Λ_+^{HF} based on the solutions of the relativistic Hartree-Fock problem, as proposed by Mittleman.⁷ In the present contribution we also explore a fourth possibility at the correlated level, which is to use the projector Λ_+^{MCSCF} based on a no-pair full MCSCF,¹⁶ which, as explained in the introduction, allows the optimization of the projection operator at the correlated level.

It may be noted that the perturbation expansion of the HF energy (8) at the 4-component relativistic level already refers to projection in that the reference state was not selected as the state with the lowest energy, rather as the lowest bound state within the energy gap between the positive- and negative-energy continua. One may further note that the two terms of the second-order relativistic HF contribution (12) have opposite signs due to the denominators and reflect the minmax principle of Talman.⁶⁸ In the present context it expresses that the relativistic HF energy is minimized with respect to κ_{ai}^{++} rotations, but maximized with respect to κ_{ai}^{-+} rotations.¹⁶ Continuing to the correlated level the second-order no-pair HF-CI contribution reads

$$E_{2:rel}^{CI} = \sum_{a+i^+} \frac{|F_{i^+a^+}^{(2)}|^2}{\varepsilon_i^+ - \varepsilon_a^+} - \frac{1}{4} \sum_{i^+j^+} \sum_{a^+b^+} \frac{|(ij||ab)|^2}{\varepsilon_a^+ + \varepsilon_b^+ - \varepsilon_i^+ - \varepsilon_j^+}, \quad (13)$$

where we explicitly indicate that all orbital energies are positive. Based on this reference the correlation energy reads

$$\begin{aligned} E_{corr:CI} &\approx E_{2:rel}^{CI} - E_{2:rel}^{HF} \\ &= -\frac{1}{4} \sum_{i^+j^+} \sum_{a^+b^+} \frac{|(ij||ab)|^2}{\varepsilon_a^+ + \varepsilon_b^+ - \varepsilon_i^+ - \varepsilon_j^+} - \sum_{a-i^+} \frac{|F_{i^+a^-}^{(2)}|^2}{\varepsilon_i^+ - \varepsilon_a^-}. \end{aligned} \quad (14)$$

It immediately becomes apparent that the correlation energy, in addition to the MP2-like correlation contribution, of negative sign, also contains a relaxation contribution, associated with orbital rotations κ_{ai}^{-+} , also of negative sign. The latter contribution can be removed by instead using a no-pair full MCSCF as reference. In the nonrelativistic domain the orbital rotations of an MCSCF using a full CI expansion become redundant and the MCSCF calculation will give the same energy as a full CI one.⁵³ However, in the relativistic domain, in the limit of a no-pair full HF-CI expansion, the κ_{ai}^{++} rotations become redundant, but not the κ_{ai}^{-+} rotations, which allow complete relaxation of the projection operator. In the [Appendix](#) we derive a perturbation expansion of the MCSCF energy using variational perturbation theory. In the present case it takes the form

$$E^{MCSCF} = \langle 0 | \hat{H}_0 | 0 \rangle + \langle 0 | \hat{H}_1 | 0 \rangle + E_2^{MCSCF} + \dots, \quad (15)$$

$$E_{2,rel}^{MCSCF} = E_{2,rel}^{HF} - \frac{1}{4} \sum_{i^+j^+} \sum_{a^+b^+} \frac{|\langle ij || ab \rangle|^2}{\varepsilon_a^+ + \varepsilon_b^+ - \varepsilon_i^+ - \varepsilon_j^+}.$$

This leads to the correlation energy

$$E_{corr:MCSCF} \approx E_{2,rel}^{MCSCF} - E_{2,rel}^{HF} = -\frac{1}{4} \sum_{i^+j^+} \sum_{a^+b^+} \frac{|\langle ij || ab \rangle|^2}{\varepsilon_a^+ + \varepsilon_b^+ - \varepsilon_i^+ - \varepsilon_j^+}, \quad (16)$$

which now only contains correlation and is as such more satisfying. On the other hand, one should note that the MCSCF-based correlation energy has a smaller magnitude than the CI-based one. This will be explored numerically in [Section IV](#).

III. COMPUTATIONAL DETAILS

A. Basis set generation

The energy-optimized basis sets, denoted dyall_1s2.Xz (with X = 2-7), were determined as follows: the SCF sets for the $1s^2$ ground states were optimized with the basis set adaption of the GRASP program^{69,70}, using the standard Gaussian model for the nucleus⁷¹, and the Dirac-Coulomb Hamiltonian. An initial set was taken for Kr from the 4z basis set of Dyall,⁷² in which the s exponent set was truncated to include only the tightest 20 functions. This set was reoptimized for the two-electron ion. Smaller sets were obtained by removing one tight function at a time and reoptimizing the basis sets. In this way, sets from 6 s to 20 s were generated. The same was done for Xe, Rn, and Uuo (using the basis sets from Refs. 72 and 73). For Ar, Ne, and He, the optimized Kr sets were used as input and the exponents were scaled and then optimized.

After generating these sets, the large component of each set was examined and compared with those of other elements, to choose basis sets that had approximately the same coefficients for the maximum of the radial wave function. The smallest set in each case was 6 s, which was used for the double-zeta (2z) set; it has three functions with large coefficients. This choice is in line with the observation that, for energy balance, the first, nodeless, shell of a given

TABLE I. Number of s functions in the SCF sets for the two-electron rare gas ions.

Basis	He	Ne	Ar	Kr	Xe	Rn	Uuo
2z	6	6	6	6	6	6	6
3z	9	9	9	10	10	10	9
4z	11	11	11	12	12	12	11
5z	13	13	14	14	14	13	12
6z	14	16	16	16	16	14	13
7z	16	18	18	18	17	16	14

angular momentum usually has one more Gaussian for the outer radial maximum than those that have nodes. Sets of s functions of 2z, 3z, 4z, 5z, 6z, and 7z quality were thereby determined. The sizes of the sets are reported in [Table I](#).

The correlating sets were optimized with the RAMCI program,⁷⁴ with common exponents for the spin-orbit components for each ℓ value. Optimizations were performed by considering single and double excitations into a virtual space that consisted of functions with a single ℓ value (and both j values). Each spinor in the correlating space was derived from a single Gaussian function, for which the large and small components were determined by diagonalization of the 2×2 Fock matrix in a Thomas-Fermi potential. The set of spinors thus derived was orthogonalized before performing the CI calculations. Optimizations were performed to produce correlating sets with up to 6 p functions, 5 d functions, 4 f functions, 3 g functions, 2 h functions, and 1 i functions. These sets were combined to form 1p, 2p1d, 3p2d1f, 4p3d2f1g, 5p4d3f2g1h, and 6p5d4f3g2h1i correlating sets for the 2z, 3z, 4z, 5z, 6z, and 7z basis sets, respectively.

The energy increments for adding functions in each angular space are presented in [Table II](#). These increments were taken from the optimizations, where only one angular momentum at a time was considered. Thus, the first value in each column is the difference from the SCF energy, the second is the difference between the correlation energy with one function and with two functions, and so on. The energy increments for each angular momentum are roughly comparable for the addition of each shell (common n). For the larger basis sets we observe that for high Z the addition of lower angular momentum functions becomes more important, whereas at lower Z it is the higher angular functions that are more important. The change in behavior starts at about Kr. Despite the overlap in the ranges of the increments for different shells, shell-wise addition of functions is probably to be preferred to a strict energy cutoff for defining the correlating sets.

B. Other computational details

All calculations in this work have been carried out using the DIRAC package for relativistic molecular calculations⁷⁵ and are based on the Dirac-Coulomb Hamiltonian. The default setting of the present release is to use the DC Hamiltonian, but to replace the expensive calculation of two-electron integrals containing small components only by a simple

TABLE II. Correlation energy increments in microhartrees (μE_h) for addition of functions in each angular space.

Atom	n	ℓ_{\max}					
		1	2	3	4	5	6
He	2	-17 826.69					
	3	-4 217.13	-2432.96				
	4	-748.21	-760.17	-604.98			
	5	-156.10	-210.77	-234.72	-205.61		
	6	-41.40	-65.22	-84.01	-92.87	-84.96	
	7	-13.67	-23.32	-32.40	-39.27	-42.86	-40.16
	Ne	2	-20 365.53				
3		-4 464.76	-2710.50				
4		-766.03	-785.07	-666.57			
5		-160.85	-208.19	-241.07	-224.79		
6		-43.58	-62.95	-82.23	-95.17	-92.25	
7		-14.57	-22.20	-30.70	-38.36	-43.84	-43.31
Ar		2	-20 467.82				
	3	-4 504.62	-2697.58				
	4	-771.94	-776.24	-657.58			
	5	-161.34	-203.52	-235.37	-219.82		
	6	-43.49	-60.82	-79.31	-92.04	-89.43	
	7	-14.47	-21.22	-29.30	-36.69	-42.08	-41.65
	Kr	2	-20 027.59				
3		-4 644.17	-2569.82				
4		-824.38	-758.18	-614.55			
5		-176.54	-201.76	-225.00	-202.88		
6		-48.15	-60.97	-77.25	-87.31	-82.08	
7		-16.20	-21.44	-29.02	-35.64	-39.91	-38.25
Xe		2	-19 252.18				
	3	-4 965.91	-2419.29				
	4	-961.75	-773.03	-578.38			
	5	-217.71	-218.30	-227.82	-193.43		
	6	-61.43	-68.71	-82.67	-89.02	-79.92	
	7	-21.46	-24.90	-32.39	-38.29	-41.26	-38.21
	Rn	2	-17 870.22				
3		-6 084.90	-2291.78				
4		-1 469.82	-891.99	-580.19			
5		-388.99	-294.68	-265.50	-206.76		
6		-123.60	-104.11	-109.37	-106.93	-90.66	
7		-47.77	-41.13	-47.37	-51.05	-51.37	-45.66
Uuo		2	-17 771.05				
	3	-8 203.67	-2505.91				
	4	-2 701.92	-1214.42	-687.20			
	5	-909.07	-496.91	-372.31	-260.02		
	6	-341.35	-208.00	-180.15	-154.14	-119.25	
	7	-146.68	-93.30	-89.02	-83.72	-75.76	-62.18

Coulombic energy correction.⁷⁶ This approximation was, however, deactivated in the present work (using the .DOSSSS keyword). The electron-nucleus interaction was described in terms of a Gaussian nuclear charge distribution

$$\rho_{nuc}^G(\mathbf{r}) = \rho_0^G \exp[-\eta r^2], \quad \rho_0^G = \left(\frac{\eta}{\pi}\right)^{3/2},$$

where the exponent was chosen so as to reproduce the empirical formula

$$\langle r_n^2 \rangle^{1/2} = [0.836 A^{1/3} + 0.570],$$

for the root mean square (rms) nuclear charge radii (in fm).^{71,77} This leads to a dependence on atomic mass numbers A in the Hamiltonian, but provides smoother basis set convergence since the (weak) singularity of the electronic wave function at nuclear origins, associated with nuclear point charges, is removed. The mass numbers used were (from He to Uuo) 4, 20, 40, 84, 132, 222, and 294.

The variational no-pair full HF-CI and full MCSCF calculations were carried out using the Kramers-restricted MCSCF module of DIRAC,^{78,79} which in turn uses the LUCIAREL CI module.^{80,81} Convergence problems were observed for the heaviest atoms and were related to optimization of positive-energy orbitals with extremely small occupation numbers (orbital rotation between a negative-energy orbital and an empty positive-energy orbital is redundant and does not change the energy at all). These problems were identified and fixed. In addition to the fully optimized Hartree-Fock calculations of the two-electron rare gas atoms we also performed calculations using the free-particle projector Λ_+^{free} as well as the bare-nucleus projector Λ_+^{bare} (keywords .FREEPJ and .VEXTPJ, respectively). In these calculations finite basis set representations of the Dirac Hamiltonian defining the projector were first built and diagonalized, and then the negative-energy solutions were projected out of the variational space in the orthonormal basis (for simplicity and numerical stability).

We also calculated second-order energy contributions to the HF, HF-CI, and MCSCF energies (Eqs. (12), (13), and (15), respectively). The second-order relativistic HF contribution was calculated using the SCF linear response module in the uncoupled mode (keyword .UNCOUP).⁸² The 2-electron Fock matrix was first constructed using the orbitals of the one-electron problem and then defined as an operator (keyword FOCKMAT). Contributions from κ_{ai}^{++} and κ_{ai}^{-+} rotations were separated using the .SKIPEP and .SKIPEE keywords, respectively. The MP2-like part of the second-order HF-CI and MCSCF correlation energies (16) was calculated using the direct MP2 module of DIRAC,⁸³ but using orbitals from the one-electron problem.

IV. RESULTS AND DISCUSSION

We first carried out relativistic HF calculations on the selected two-electron atoms using different projection operators. The results are compiled in Table III. With respect to the reference Λ_+^{HF} projector, one sees that the free-particle projector Λ_+^{free} shows very poor performance, giving errors of -20 mE_{*h*} for Ne⁸⁺ and exploding to -2677 E_{*h*} for Uuo¹¹⁶⁺, in line with the theoretical analysis of Heully *et al.*⁵ and previous numerical results.⁶ The bare-nucleus projector Λ_+^{bare} , on the other hand, is a good approximation to Λ_+^{HF} , giving an error less than -10 mE_{*h*} for an atom as heavy as Uuo¹¹⁶⁺. This is not that surprising since the shielding of the nuclear charge by the other $1s_{1/2}$ electron is only approximately 0.3 according to Slater's rules.⁸⁴ Still according to Slater's rules, the shielding of $1s_{1/2}$ electrons will be the same in the neutral atoms, whereas the shielding will be more significant for outer shells. However,

TABLE III. Hartree-Fock energies (in E_{*h*}) of the two-electron rare gas atoms based on the Dirac-Coulomb Hamiltonian using different projection operators and the dyall_1s2.6z basis.

Z	DC(Λ_+^{HF})	DC(Λ_+^{bare})	DC(Λ_+^{free})
2	-2.861 813	-2.861 813	-2.861 820
10	-93.982 761	-93.982 762	-94.002 680
18	-314.199 521	-314.199 525	-314.513 907
36	-1 296.165 168	-1 296.165 234	-1 303.570 815
54	-3 002.947 488	-3 002.947 788	-3 049.385 180
86	-8 245.261 661	-8 245.263 456	-8 674.425 715
118	-18 090.944 596	-18 090.952 854	-20 767.807 429

the deviation from the bare-nucleus situation for outer shells will be compensated by the reduction of relativistic effects as one moves from core to valence. The bare-nucleus projector is therefore expected to be a good approximation to Λ_+^{HF} also for the neutral atoms, as shown in Table 1 of Ref. 6. Under all circumstances, there is no computational savings achieved through the use of Λ_+^{bare} , so the Λ_+^{HF} projector is clearly to be preferred in 4-component HF calculations. In passing one may also note that 4-component calculations based on the projectors Λ_+^{free} and Λ_+^{bare} mimic the use of the 2-component first-order Douglas-Kroll-Hess (DKH1)⁸⁵⁻⁸⁷ and eXact 2-Component (X2C)⁸⁸⁻⁹⁰ Hamiltonians, respectively, and illustrate their relative performance (the second-order DKH2 Hamiltonian is closer to X2C than to DKH1).^{6,91}

We now turn to correlated calculations. It was noted by Tatewaki and Watanabe¹⁴ that no-pair full CI results for the helium isoelectronic series differed according to whether the positive-energy orbitals were generated from a HF calculation or by diagonalization of the Dirac Hamiltonian. At the no-pair full CI level the latter results can be reproduced by carrying out a HF calculation using the bare-nucleus projector Λ_+^{bare} , as above. The dependence of the no-pair full CI results on the choice of projector is easily understood since the separation of the positive- and negative-energy space depends on the potential. We argue, in line with Mittleman⁷ as well as Saue and Visscher,¹⁶ that any ambiguity is removed by optimizing the projectors to the actual potential experienced by the electrons.

In Table IV we report total energies of the two-electron rare gas atoms obtained at different levels of theory using the dyall_1s2.6z basis. Results for all basis sets dyall_1s2.Xz (with X = 2-7) are given in the supplementary material.¹¹³ We remind the reader that these results are obtained with a Gaussian model for the nuclear charge distribution.⁷¹ In Table V and Figure 2 we show the corresponding correlation energies. We first note that the nonrelativistic correlation energy is close to the reference value $-0.046 67$ E_{*h*} of Eq. (3). The deviation is in part due to the use of a Gaussian nucleus in the present calculations. The nonrelativistic correlation energy is, however, not constant with respect to nuclear charge, as suggested by Eq. (3). This is easily understood as an artifact of our calculations, since we have used basis sets optimized for relativistic calculations that thereby become increasingly poor for the heavier atoms. Indeed, we see that the correlation energy is reduced as a function of nuclear charge, in line

TABLE IV. Total energies (in E_h) of the two-electron rare gas atoms using the dyall_1s2.6z basis.

Z	Nonrelativistic		4-component relativistic (DC)		
	HF	CI	HF	HF-CI	MCSCF
2	-2.861 680	-2.903 452	-2.861 813	-2.903 585	-2.903 585
10	-93.861 077	-93.906 282	-93.982 761	-94.027 915	-94.027 913
18	-312.860 496	-312.906 101	-314.199 521	-314.244 994	-314.244 978
36	-1 273.597 042	-1 273.642 893	-1 296.165 168	-1 296.210 997	-1 296.210 809
54	-2 882.268 657	-2 882.314 567	-3 002.947 488	-3 002.994 523	-3 002.993 873
86	-7 341.554 142	-7 341.599 913	-8 245.261 661	-8 245.316 411	-8 245.313 992
118	-13 846.936 084	-13 846.980 364	-18 090.944 596	-18 091.033 473	-18 091.025 293

TABLE V. Correlation energies (in E_h) of the two-electron rare gas atoms using the dyall_1s2.6z basis and different models. $\Delta_{MC/CI}$ is the difference in correlation energy between the MCSCF and HF-CI. NR: nonrelativistic; R: relativistic.

Z	Variational				Perturbative		
	CI(NR)	HF-CI(R)	MCSCF(R)	$\Delta_{MC/CI}$	HF-CI(R)	MCSCF(R)	$\Delta_{MC/CI}$
2	-0.041 772	-0.041 772	-0.041 772	0.000 000	-0.046 025	-0.046 025	0.000 000
10	-0.045 205	-0.045 154	-0.045 152	0.000 002	-0.046 040	-0.046 039	0.000 001
18	-0.045 605	-0.045 473	-0.045 457	0.000 016	-0.045 963	-0.045 953	0.000 010
36	-0.045 851	-0.045 829	-0.045 641	0.000 188	-0.046 198	-0.046 061	0.000 136
54	-0.045 910	-0.047 035	-0.046 385	0.000 650	-0.047 816	-0.047 202	0.000 615
86	-0.045 771	-0.054 750	-0.052 331	0.002 419	-0.058 574	-0.054 931	0.003 642
118	-0.044 280	-0.088 877	-0.080 697	0.008 180	-0.106 101	-0.089 368	0.016 733

with the minimization principle of nonrelativistic theory. The relativistic correlation energy obtained using no-pair full HF-CI as reference is clearly not constant with respect to nuclear charge, but agrees well with the energies reported by Watanabe and Tatewaki⁴⁶ (indicated by the dashed line in Figure 2), who used a uniformly charged sphere model for the nuclear charge distribution. As discussed in Section II C, a constant correlation energy can only be obtained by scaling of the speed of light. The relativistic correlation energy obtained using the no-pair full MCSCF is smaller than the full HF-CI counterpart, in agreement with the theoretical analysis of Section II C as well as the minmax principle of relativistic SCF.^{16,68} The difference between the correlation energies obtained with no-pair full HF-CI and full MCSCF stays below 10 m E_h . However, for Rn⁸⁴⁺ it amounts to about 530 cm⁻¹, and it would be interesting to know the impact of such an energy difference when calculating QED effects.

In Table V we also report approximate correlation energies calculated according to formulas (14) and (16). These values agree quite well with the ones obtained by variational calculations (perhaps with the exception of the full HF-CI correlation energy for Uuo¹¹⁶⁺) and confirm the relevance of the theoretical analysis in Section II.

Since we have a systematic series of correlation-consistent basis sets at our disposal, we may investigate the convergence of the HF-CI and full MCSCF correlation energies in terms of the one-electron basis. From the nonrelativistic domain the convergence is known to be painstakingly slow due to the presence of a cusp at the point of coalescence of two electrons,⁹² prompting the comment: “We may regard the standard CI approach as a brave attempt

to expand the nondifferentiable interelectronic distance r_{12} in products of one-electron functions.”⁹³ Schwartz found that the partial wave increment of the second-order energy of the $1/Z$ expansion (9) is to leading order proportional to $(\ell + 1/2)^{-4}$,^{94,95} a result generalized to the variational case by Hill.⁹⁶ This result implies that the truncation error is to leading order $(\ell + 1)^{-3}$, that is, it has an inverse cubic scaling with respect to the lowest angular momentum value absent in the partial wave expansion. Klopper and co-workers,⁹⁷ on the other hand, suggested, based on observations by Carroll *et al.*,⁹⁸ that the truncation error in an expansion of the exact

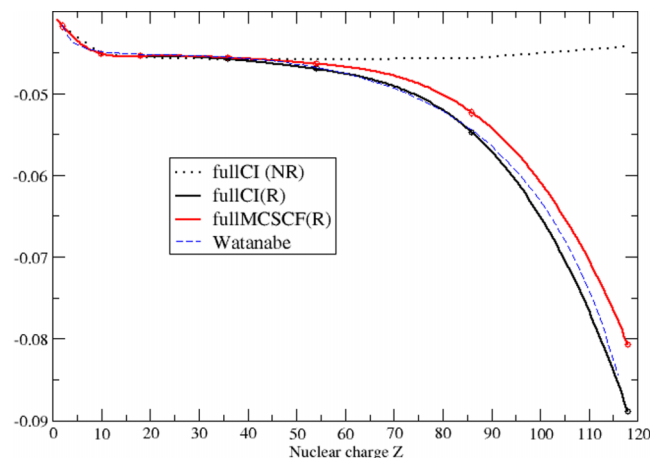


FIG. 2. Correlation energies (in E_h) of the two-electron rare gas atoms as a function of nuclear charge Z , using the dyall_1s2.6z basis. NR: nonrelativistic; R: relativistic. The blue dashed line refers to fullCI results (best estimate) of Watanabe and Tatewaki.⁴⁶

TABLE VI. Fits of HF-CI and full MCSCF correlation energies (in E_h) to the formula $E_{corr,X} = E_{corr,\infty} + aX^{-b}$, where X is the cardinal number of the dyall_1s2.Xz basis set. Corr.cf. = correlation coefficient.

Z	HF-CI				full MCSCF			
	$E_{corr,\infty}$	a	b	Corr.cf.	$E_{corr,\infty}$	a	b	Corr.cf.
2	-0.042 120	0.057 06	2.8761	0.999 98	-0.042 098	0.057 76	2.8976	0.999 98
10	-0.045 781	0.065 12	2.5963	0.999 96	-0.045 779	0.065 13	2.5966	0.999 96
18	-0.046 121	0.066 41	2.5892	0.999 95	-0.046 102	0.066 55	2.5926	0.999 95
36	-0.046 486	0.067 85	2.5943	0.999 95	-0.046 303	0.069 00	2.6161	0.999 95
54	-0.047 756	0.068 87	2.5515	0.999 94	-0.047 128	0.070 83	2.5767	0.999 98
86	-0.055 768	0.072 14	2.3652	0.999 92	-0.053 210	0.080 89	2.4900	0.999 79
118	-0.091 747	0.074 22	1.8187	0.999 24	-0.082 685	0.089 07	2.0924	0.999 84

helium ground state function in terms of orbital principal quantum number n scales as n^{-3} , a result further corroborated by Kutzelnigg.⁹⁹ Although the definition of the principal quantum number for a general molecular orbital is less than obvious, the principal expansion is useful in that it corresponds closely to the construction of correlation-consistent basis sets, where basis functions are added in shell-wise fashion such that the cardinal number X may be associated with the principal quantum number n . Indeed, successful basis set extrapolation schemes have been based on the approximate formula¹⁰⁰⁻¹⁰²

$$E_{corr,X} = E_{corr,\infty} + aX^{-3}.$$

When the nonrelativistic electronic Hamiltonian is replaced by the Dirac-Coulomb Hamiltonian, the correlation cusp is replaced by a weak singularity,^{103,104} analogous to what is observed at the point of coalescence of an electron and a point nucleus. One may therefore expect slower convergence of the correlation energy with respect to the one-electron basis. Salomonsen and Öster¹⁰⁵ found that the partial wave increment of the ground-state helium correlation energy, in a calculation equivalent to the use of the Dirac-Coulomb Hamiltonian with bare-nucleus projectors Λ_+^{bare} , goes as $(\ell + 1/2)^{-2}$ and indeed much slower than the corresponding nonrelativistic expansion. Kutzelnigg *et al.*^{106,107} arrived at the same result in the framework of direct perturbation theory. Of interest in the present context is also the computational study by Halkier *et al.* who found that the basis-set convergence of the correlation contribution to the two-electron Darwin term in nonrelativistic calculations obeyed a X^{-1} scaling with respect to the cc-pVXZ basis sets.¹⁰⁸ Based on the above observations, we have fitted the HF-CI and full MCSCF correlation energies, given in the supplementary material,¹¹³ to the formula

$$E_{corr,X} = E_{corr,\infty} + aX^{-b}.$$

The results of the fits are given in Table VI. In all cases the correlation coefficient¹⁰⁹ is close to one and the listed value of $E_{corr,\infty}$ may be considered our best estimate for the correlation energy. In the case of HF-CI, the fitted exponent b for helium is close to three, but reduces to 1.72 for Uuo¹¹⁶⁺. This is clearly better than the X^{-1} behaviour suggested by previous studies. In the case of full MCSCF the convergence is even faster, corresponding to X^{-2} . As such this is good news for relativistic correlated calculations, but the notable variation of the fit parameters for different Z calls for further study.

V. CONCLUSIONS AND PERSPECTIVES

The goal of the present work is to provide a proper definition of electron correlation energy within a well-defined model for relativistic molecular calculations, which is the no-pair approximation. Present-day relativistic molecular electronic structure calculations treat the negative-energy orbitals as an orthogonal complement which is continuously updated at the SCF level and frozen at the correlated level. We argue, however, as did Mittleman⁷ as well as Saue and Visscher,¹⁶ that the projectors in which the Dirac-Coulomb Hamiltonian is embedded should be optimized also at the correlated level. This is possible with a no-pair full MCSCF calculation, that is, an MCSCF calculation based on a no-pair full CI expansion, but including orbital rotations κ_{ai}^{++} between positive-energy occupied orbitals and negative-energy virtual orbitals. By theoretical analysis based on variational perturbation theory we find that the energy difference with respect to Hartree-Fock is, to the lowest order, a pure MP2-like correlation contribution, whereas using no-pair full HF-CI as reference leads to an additional relaxation contribution associated with the κ_{ai}^{++} rotations. Calculations on the two-electron rare gas atoms show that full optimization of the projection operator

$$\Lambda_+^{HF} \rightarrow \Lambda_+^{MCSCF}$$

reduces the correlation energy in accordance with the underlying minmax-principle and our theoretical analysis. We may add that such optimization is also possible within a truncated no-pair MCSCF, but will require inclusion of orbital rotations κ_{ai}^{++} involving positive-energy virtual orbitals, since they are no longer redundant. We would also like to stress that no-pair full MCSCF, rather than no-pair full CI, provides the reference correlation energy in the relativistic domain also when two-electron terms beyond the instantaneous Coulomb interaction, such as the Gaunt or Breit terms, are added. We plan to explore this in future work.

An interesting observation from the present study is that the relativistic correlation energy, obtained by no-pair full MCSCF calculations, scales at worst as X^{-2} in terms of the cardinal number of the dyall_1s2.Xz basis sets optimized for the two-electron atoms. This is certainly more promising than the X^{-1} scaling suggested in previous studies, but slower than the X^{-3} observed in the nonrelativistic domain. The basis set convergence can be significantly improved

by switching to explicitly correlated methods.^{39–41} However, the formulation of such methods within the relativistic no-pair approximation is less straightforward due to the need to eliminate determinants that lead to continuum dissolution, yet recently promising steps have been taken in this direction.^{104,110}

For the helium isoelectronic series the correlation energy is not, to the lowest order, independent of nuclear Z , as in the nonrelativistic domain.⁴⁶ Our analysis suggests that coordinate scaling (7) should be accompanied by velocity scaling. In the nonrelativistic domain this comes about automatically and leads to the well-known $1/Z$ expansion for the correlation energy, whereas explicit scaling of the speed of light would be necessary in the relativistic domain.

A challenge for future work is to reproduce the correlation energies obtained at the no-pair full MCSCF level and shown in Figure 2 using coupled cluster (CC) theory. This would require inclusion of the relaxation of the negative-energy orbitals in CC calculations, without explicit correlation of these orbitals. Such relaxation is also necessary for calculations of magnetic properties based on response theory.²⁶ In a longer perspective we would also like to go beyond the no-pair approximation and connect modern relativistic quantum chemical variational methods to QED.

ACKNOWLEDGMENTS

Computing time from CALMIP (Calcul en Midi-Pyrénées) is gratefully acknowledged. A.A. was financially supported by a PhD-grant from the Syrian Ministry of Education as well as kind support from Université Toulouse III. We dedicate this paper to Werner Kutzelnigg (Bochum) for his outstanding contributions to our present-day understanding of both relativity and electron correlation in molecular quantum mechanics.

APPENDIX: VARIATIONAL PERTURBATION THEORY

1. Introduction

In the following we shall employ variational perturbation theory as defined by Helgaker and Jørgensen⁴⁹ and which underpins modern response theory: we start from a Hamiltonian

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1$$

parametrized in terms of a perturbation strength λ . We seek a variational solution in terms of some suitable trial function Φ with variational parameters collected in the vector ξ and such that the energy, defined as the expectation value of the Hamiltonian, becomes a function of those, that is

$$E \equiv E(\xi) = E_0 + \lambda E_1, \quad E_k = \langle \Phi(\xi) | \hat{H}_k | \Phi(\xi) \rangle.$$

A key ingredient of variational perturbation theory is the assumption that the energy is optimized for any value of the perturbation strength, that is

$$\left. \frac{\partial E}{\partial \xi_i} \right|_{\lambda} = 0, \quad (\text{A1})$$

which implies that the optimal values ξ of the variational parameters are functions of the perturbation strength

$$\xi \equiv \xi(\lambda).$$

We write the perturbation expansion of the energy as a Taylor series with respect to $\lambda = 0$

$$E(\lambda) = E_0 + \left. \frac{dE}{d\lambda} \right|_{\lambda=0} \lambda + \frac{1}{2} \left. \frac{d^2E}{d\lambda^2} \right|_{\lambda=0} \lambda^2 + \dots$$

such that the n th-order correction to the energy is expressed in terms of the n th-order total energy derivative at zero field strength. Explicit expressions for the first two derivatives are

$$\begin{aligned} \left. \frac{dE}{d\lambda} \right|_{\lambda=0} &= \left[\frac{\partial E}{\partial \lambda} + \sum_i \frac{\partial E}{\partial \xi_i} \frac{d\xi_i}{d\lambda} \right]_{\lambda=0} = \left. \frac{\partial E}{\partial \lambda} \right|_{\lambda=0}, \\ \left. \frac{d^2E}{d\lambda^2} \right|_{\lambda=0} &= \left[\frac{\partial^2 E}{\partial \lambda^2} + \sum_i \frac{\partial^2 E}{\partial \lambda \partial \xi_i} \frac{d\xi_i}{d\lambda} + \sum_i \frac{\partial E}{\partial \xi_i} \frac{d^2 \xi_i}{d\lambda^2} \right]_{\lambda=0} \\ &= \left[\frac{\partial^2 E}{\partial \lambda^2} + \sum_i \frac{\partial^2 E}{\partial \lambda \partial \xi_i} \frac{d\xi_i}{d\lambda} \right]_{\lambda=0}, \end{aligned}$$

where the simplifications are due to the variational condition (A1). Further simplifications are obtained by assuming that the trial function has no explicit dependence on the perturbation strength

$$\begin{aligned} \left. \frac{dE}{d\lambda} \right|_{\lambda=0} &= \langle \Phi(\mathbf{0}) | \hat{H}_1 | \Phi(\mathbf{0}) \rangle, \\ \left. \frac{d^2E}{d\lambda^2} \right|_{\lambda=0} &= \left[\sum_i \frac{\partial E_1}{\partial \xi_i} \right]_{\lambda=0} \xi_i^{[1]}, \quad \xi_i^{[n]} = \left. \frac{d^n \xi_i}{d\lambda^n} \right|_{\lambda=0}. \end{aligned}$$

The first-order energy obeys the Hellmann-Feynman theorem.

The n th-order variational parameters $\xi^{[n]}$ are in turn determined from the variational condition (A1). For instance, the first-order variational parameters are determined by

$$\left[\frac{d}{d\lambda} \left(\frac{\partial E}{\partial \xi_i} \right) \right]_{\lambda=0} = \left[\frac{\partial^2 E}{\partial \lambda \partial \xi_i} + \sum_j \frac{\partial^2 E}{\partial \xi_i \partial \xi_j} \frac{d\xi_j}{d\lambda} \right]_{\lambda=0} = 0, \quad (\text{A2})$$

which simplifies to

$$\left[\frac{\partial E_1}{\partial \xi_i} + \sum_j \frac{\partial^2 E_0}{\partial \xi_i \partial \xi_j} \xi_j^{[1]} \right]_{\lambda=0} = 0, \quad (\text{A3})$$

when there is no explicit dependence of the trial function on the perturbation strength λ . We may recast the latter expression on matrix form as

$$E_0^{[2]} \xi^{[1]} = -E_1^{[1]},$$

where appears the Hessian matrix $E_0^{[2]}$ and the gradient vector $E_1^{[1]}$ with elements

$$E_{0;ij}^{[2]} = \left. \frac{\partial^2 E_0}{\partial \xi_i \partial \xi_j} \right|_{\lambda=0}, \quad E_{1;i}^{[1]} = \left. \frac{\partial E_1}{\partial \xi_i} \right|_{\lambda=0}.$$

The variational parameters obey the $(2n+1)$ rule in that variational parameters to order n define the energy through order $(2n+1)$. In passing it may be interesting to note that whereas the $(2n+1)$ rule is attributed to Wigner

(1935),¹¹¹ Hylleraas was clearly aware of it five years earlier.^{51,112}

2. Two-electron atoms

In Secs. 3–5 of the Appendix we restrict attention to two-electron atoms and partition the electronic Hamiltonian according to the Hylleraas scheme. In second quantization the zeroth- and first-order Hamiltonians read

$$\hat{H}_0 = \sum_{pq} h_{pq} \hat{p}^\dagger \hat{q}, \quad (\text{A4})$$

$$\hat{H}_1 = \frac{1}{4} \sum_{pqrs} \langle pr \parallel qs \rangle \hat{p}^\dagger \hat{r}^\dagger \hat{s} \hat{q}, \quad (\text{A5})$$

with the antisymmetrized two-electron integrals in Dirac notation

$$\langle pr \parallel qs \rangle = \langle pr | qs \rangle - \langle pr | sq \rangle.$$

In the following we shall consider three variational methods: Hartree-Fock (HF), Configuration Interaction (CI), and Multiconfigurational SCF (MCSCF), where the former two may be considered as special cases of the latter. We shall employ exponential parametrizations which preserve the normalization of the reference (zero-field) solution and thereby allow unconstrained optimization techniques (no Lagrange multipliers). They furthermore allow straightforward identification and elimination of redundant variational parameters, that is, parameters whose values do not change the energy or whose effect can be described as a linear combination of other parameters.

3. Hartree-Fock

The Hartree-Fock trial function is parametrized in terms of the orbital rotation operator^{54–56} $\hat{\kappa}$

$$|HF\rangle = \exp[-\hat{\kappa}] |0\rangle, \quad \hat{\kappa} = \sum_{pq} \kappa_{pq} \hat{p}^\dagger \hat{q}, \quad (\text{A6})$$

where the matrix κ is anti-Hermitian ($\kappa_{pq} = -\kappa_{qp}^*$) to assure unitarity of the exponential operator. Here and in the following indices i, j, k, l, \dots refer to occupied orbitals, indices a, b, c, d, \dots refer to virtual orbitals, and indices p, q, r, s, \dots refer to general orbitals. In terms of non-redundant parameters the orbital rotation operator is expressed as

$$\hat{\kappa} = \sum_{ai} (\kappa_{ai} \hat{a}^\dagger \hat{i} - \kappa_{ai}^* \hat{i}^\dagger \hat{a}).$$

Using the Baker-Campbell-Hausdorff (BCH) expansion an expansion of the energy in orders of the variational parameters $\{\kappa_{pq}\}$ is obtained

$$E^{HF} = \langle 0 | \exp[\hat{\kappa}] \hat{H} \exp[-\hat{\kappa}] | 0 \rangle = \langle 0 | \hat{H} | 0 \rangle + \langle 0 | [\hat{\kappa}, \hat{H}] | 0 \rangle + \frac{1}{2} \langle 0 | [[\hat{\kappa}, [\hat{\kappa}, \hat{H}]]] | 0 \rangle + O(\kappa_{pq}^3),$$

which simplifies the calculation of energy derivatives. Further simplification is obtained by noting that⁵³

$$\tilde{H} = [\hat{\kappa}, \hat{H}] = \sum_{pq} \tilde{h}_{pq} \hat{p}^\dagger \hat{q} + \frac{1}{4} \sum_{pqrs} \langle pr \parallel qs \rangle \hat{p}^\dagger \hat{r}^\dagger \hat{s} \hat{q}, \quad (\text{A7})$$

where appear one-index transformed integrals

$$\tilde{h}_{pq} = \sum_t \{ \kappa_{pt} h_{tq} - h_{pt} \kappa_{tq} \},$$

$$\langle pr \parallel qs \rangle = \sum_t \{ (\kappa_{pt} \langle tr \parallel qs \rangle - \langle pr \parallel ts \rangle \kappa_{tq}) + (\kappa_{rt} \langle pt \parallel qs \rangle - \langle pr \parallel qt \rangle \kappa_{tq}) \}.$$

The HF energy expectation value may therefore be expressed as a sum of expectation values of increasingly nested Hamiltonians

$$E^{HF} = \langle 0 | \hat{H} | 0 \rangle + \langle 0 | \tilde{H} | 0 \rangle + \frac{1}{2} \langle 0 | \tilde{\tilde{H}} | 0 \rangle + O(\kappa_{pq}^3),$$

all with the same structure

$$\langle 0 | \hat{H} | 0 \rangle = \sum_i h_{ii} + \frac{1}{2} \sum_{ij} \langle ij \parallel ij \rangle,$$

but expressed in terms of increasingly transformed integrals.

With our specific choice of zeroth-order Hamiltonian the HF Hessian matrix is given by

$$E_0^{HF[2]} = \begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix},$$

$$A_{ai,bj} = \left. \frac{\partial^2 E_0^{HF}}{\partial \kappa_{ai}^* \partial \kappa_{bj}} \right|_{\lambda=0} = \delta_{ab} \delta_{ij} (\varepsilon_a - \varepsilon_i) \quad (\text{A8})$$

$$B_{ai,bj} = \left. \frac{\partial^2 E_0^{HF}}{\partial \kappa_{ai}^* \partial \kappa_{bj}^*} \right|_{\lambda=0} = 0.$$

The HF gradient vector takes the form

$$E_1^{HF[1]} = \begin{bmatrix} \mathbf{g} \\ \mathbf{g}^* \end{bmatrix}, \quad g_{ai} = \left. \frac{\partial E_1^{HF}}{\partial \kappa_{ai}^*} \right|_{\lambda=0} = -F_{ai}^{(2)},$$

where appear elements of the two-electron Fock matrix

$$F_{pq}^{(2)} = \sum_j \langle pj \parallel qj \rangle, \quad (\text{A9})$$

albeit with the important difference that it is expressed in terms of the orbitals of the one-electron system. The second-order HF energy therefore reads

$$E_2^{HF} = \frac{1}{2} \left. \frac{d^2 E^{HF}}{d\lambda^2} \right|_{\lambda=0} = \sum_{ai} \frac{|F_{ia}^{(2)}|^2}{\varepsilon_i - \varepsilon_a}.$$

In the nonrelativistic case each individual term of the second-order contribution is negative, reflecting that orbital relaxation lowers the total energy.

4. Configuration interaction

The CI trial function is parametrized in terms of the state transfer operator⁵⁷ \hat{S}

$$|CI\rangle = \exp[-\hat{S}] |0\rangle, \quad (\text{A10})$$

$$\hat{S} = \sum_{M \in \{|M\rangle\} \setminus \{|0\rangle\}} (s_M |M\rangle \langle 0| - s_M^* |0\rangle \langle M|),$$

where the summation runs over the elements of the N -particle (determinant) basis $\{|M\rangle\}$ excluding the reference determinant $|0\rangle$. The CI Hessian is given by

$$E_0^{CI[2]} = \begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix},$$

$$A_{M,N} = \left. \frac{\partial^2 E_0^{CI}}{\partial s_M^* \partial s_N} \right|_{\lambda=0} = \delta_{MN} (E_M - E_0) \quad (\text{A11})$$

$$B_{M,N} = \left. \frac{\partial^2 E_0^{CI}}{\partial s_M^* \partial s_N^*} \right|_{\lambda=0} = 0$$

whereas the CI gradient assumes the form

$$E_1^{CI[1]} = \begin{bmatrix} \mathbf{g} \\ \mathbf{g}^* \end{bmatrix}, \quad g_M = \left. \frac{\partial E_1^{CI}}{\partial s_M^*} \right|_{\lambda=0} = -\langle M | \hat{H}_1 | 0 \rangle.$$

Using these expressions and solving the first-order response equation we find that the second-order CI energy may be expressed as

$$E_2^{CI} = \left. \frac{1}{2} \frac{d^2 E^{CI}}{d\lambda^2} \right|_{\lambda=0} = - \sum_{M \neq 0} \frac{\langle 0 | \hat{H}_1 | M \rangle \langle M | \hat{H}_1 | 0 \rangle}{E_M - E_0}.$$

Since \hat{H}_1 is a two-electron operator, $\langle 0 | \hat{H}_1 | M \rangle$ can only be non-zero for singly or doubly excited determinants $|M\rangle$, and we may recast the above expression as

$$E_2^{CI} = - \sum_{ia} \frac{\langle 0 | \hat{H}_1 | 0_i^a \rangle \langle 0_i^a | \hat{H}_1 | 0 \rangle}{E_i^a - E_0}$$

$$- \frac{1}{4} \sum_{ij} \sum_{ab} \frac{\langle 0 | \hat{H}_1 | 0_{ij}^{ab} \rangle \langle 0_{ij}^{ab} | \hat{H}_1 | 0 \rangle}{E_{ij}^{ab} - E_0}$$

$$= \sum_{ai} \frac{|F_{ia}^{(2)}|^2}{\varepsilon_i - \varepsilon_a} - \frac{1}{4} \sum_{ij} \sum_{ab} \frac{|\langle ij || ab \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}.$$

The first term can be recognized as the second-order HF energy and therefore cancels out when considering the nonrelativistic CI correlation energy. To the lowest order we thus obtain

$$E_{corr,2}^{CI} = E_2^{CI} - E_2^{HF} = -\frac{1}{4} \sum_{ij} \sum_{ab} \frac{|\langle ij || ab \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j},$$

which is identical to the second-order Møller-Plesset energy, but with the important difference that it is expressed in the orbitals of the one-electron problem.

5. Multiconfigurational SCF

The MCSCF trial function is parametrized in terms of both $\hat{\kappa}$ and \hat{S}

$$|MC\rangle = \exp[-\hat{\kappa}] \exp[-\hat{S}] |0\rangle. \quad (\text{A12})$$

In the present case the MCSCF gradient is given by

$$E_1^{MCSCF[1]} = \begin{bmatrix} \mathbf{g}_o \\ \mathbf{g}_o^* \\ \mathbf{g}_c \\ \mathbf{g}_c^* \end{bmatrix}, \quad g_{o,ai} = \left. \frac{\partial E_1^{MCSCF}}{\partial \kappa_{ai}^*} \right|_{\lambda=0} = -F_{ai}^{(2)},$$

$$g_{c,M} = \left. \frac{\partial E_1^{MCSCF}}{\partial s_M^*} \right|_{\lambda=0} = -\langle M | \hat{H}_1 | 0 \rangle,$$

whereas the MCSCF Hessian assumes the structure

$$E_0^{MCSCF[2]} = \begin{bmatrix} E_{0;oo}^{[2]} & E_{0;oc}^{[2]} \\ E_{0;co}^{[2]} & E_{0;cc}^{[2]} \end{bmatrix}.$$

In the present case the pure orbital part $E_{oo}^{[2]}$ and the pure configurational part $E_{cc}^{[2]}$ are analogous to the HF Hessian (A8) and CI Hessian (A11), respectively, whereas the mixed orbital-configurational part $E_{oc}^{[2]}$ is given by

$$E_{0;oc}^{MCSCF[2]} = \begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix}, \quad A_{ai,N} = \left. \frac{\partial^2 E_0^{MCSCF}}{\partial \kappa_{ai}^* \partial s_N} \right|_{\lambda=0} = \langle 0_i^a | N \rangle (E_i^a - E_0) = \langle 0_i^a | N \rangle (\varepsilon_a - \varepsilon_i)$$

$$B_{ai,N} = \left. \frac{\partial^2 E_0^{MCSCF}}{\partial \kappa_{ai}^* \partial s_N^*} \right|_{\lambda=0} = 0.$$

The corresponding response equations are

$$\sum_{bj} A_{ai,bj} \kappa_{bj}^{(1)} + \sum_{bj} B_{ai,bj} \kappa_{bj}^{(1)*} + \sum_N A_{ai,N} s_N^{(1)} + \sum_N B_{ai,N} s_N^{(1)*} = -g_{ai},$$

$$\sum_{bj} A_{M,bj} \kappa_{bj}^{(1)} + \sum_{bj} B_{M,bj} \kappa_{bj}^{(1)*} + \sum_N A_{M,N} s_N^{(1)} + \sum_N B_{M,N} s_N^{(1)*} = -g_M,$$

and their complex conjugate partners. They translate into

$$(\varepsilon_a - \varepsilon_i) \kappa_{ai}^{(1)} + \sum_N \langle 0_i^a | N \rangle (\varepsilon_a - \varepsilon_i) s_N^{(1)} = F_{ai}^{(2)},$$

$$\sum_{bj} \langle M | 0_j^b \rangle (\varepsilon_b - \varepsilon_j) \kappa_{bj}^{(1)} + (E_M - E_0) s_M^{(1)} = \langle M | \hat{H}_1 | 0 \rangle.$$

For $|M\rangle = |0_i^a\rangle$ the above two equations become identical, showing that if both the determinant $|M\rangle = |0_i^a\rangle$ is present in the CI-expansion of the MCSCF trial function and the orbital rotation operator κ_{ai} is included, then linear dependency will occur in the first-order response equation, indicating the possible presence of redundant variational parameters. Generally it is known that if the N -particle basis $\{|M\rangle\}$ is complete, then the orbital rotation parameters $\{\kappa_{pq}\}$ become redundant.⁵³ In the case of no-pair full MCSCF the κ_{ai}^{++} rotations are redundant, but not the κ_{ai}^{-+} rotations. The former parameters are accordingly excluded, whereas the response equation for the latter simplifies to

$$(\varepsilon_a^- - \varepsilon_i^+) \kappa_{ai}^{(1)-+} = F_{a^-i^+}^{(2)}$$

The second-order MCSCF energy is then given by

$$E_{2;rel}^{MCSCF} = E_{2;rel}^{HF} - \frac{1}{4} \sum_{i^+j^+} \sum_{a^+b^+} \frac{|(ij||ab)|^2}{\varepsilon_a^+ + \varepsilon_b^+ - \varepsilon_i^+ - \varepsilon_j^+}$$

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