

# **Ab initio MCDHF calculations of electron-nucleus interactions**

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## Abstract

We present recent advances in the development of atomic *ab initio* multiconfiguration Dirac-Hartree-Fock (MCDHF) theory, implemented in the GRASP relativistic atomic structure code. For neutral atoms, the deviations of properties calculated within the Dirac-Hartree-Fock method (based on independent particle model of an atomic cloud) are usually dominated by electron correlation effects, i. e. the non-central interactions of individual electrons. We present the recent advances in accurate calculations of electron correlation effects in small, medium, and heavy neutral atoms. We describe methods of systematic development of multiconfiguration expansions leading to systematic, controlled improvement of the accuracy of the *ab initio* calculations. These methods originate from the concept of the Complete Active Space model within the Dirac-Hartree-Fock theory, which, at least in principle, permits fully relativistic calculations with full account of electron correlation effects. The calculations within the Complete Active Space model on currently available computer systems are feasible only for very light systems. For heavier atoms or ions with more than a few electrons, restrictions have to be imposed on the multiconfiguration expansions. We present methods and tools, which are designed to extend the numerical calculations in a controlled manner, where multiconfiguration expansions account for all leading electron correlation effects. We show examples of applications of the GRASP code to calculations of hyperfine structure constants, but the code may be used for calculations of arbitrary bound-state atomic properties. In recent years it has been applied to calculations of atomic and ionic spectra (transition energies and rates), to determinations of nuclear electromagnetic moments, as well as to calculations related to interactions of bound electrons with nuclear electromagnetic moments leading to violations of discrete symmetries.

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## I. INTRODUCTION

Atoms are the fundamental constituents of matter, at least on a certain level of our understanding, and there are several good reasons to pursue the research into their structure and dynamics. The physical laws that govern the behaviour of electrons in an atom are not known exactly, but to a certain approximation (according to Karl Popper, the probability that a scientific theory will never become superseded, is zero [1]). The algebraic formulation of these laws was laid in 1925 by Werner Heisenberg (matrix mechanics [2]), a few months later by Erwin Schrödinger (wave mechanics [3]), and by Paul Adrien Maurice Dirac (quantum mechanics [4]). The relativistically invariant electron wave equation was discovered in 1928 by Dirac [5]. The subject of the research described in this work is the determination of numerical solutions of the equations which arise from these approximate laws. All measurable properties of an isolated atom can, in principle, be obtained from these solutions, although some approximations break down for highly excited states. One of the immediate applications of such solutions is a comparison with accurate, experimentally determined atomic properties, from which a better understanding of the quantum electrodynamical interactions inside an atom can be gained [6, 7]. The electronic cloud shapes itself primarily in response to the interactions with the Coulomb field originating from the atomic nucleus and to the electron-electron interactions. Knowledge of this shape is necessary to detect and extract higher-order electromagnetic interactions, such as hyperfine structure [8, 9], isotope shifts [10], and weak interactions [11–13]. Apart from basic interest, atomic data are of significant importance in several other fields. Most of our knowledge about the stars and the interstellar medium is based on the analysis of stellar spectra. Computational atomic physics has been one of the primary sources of spectral data for astrophysics [14], but the demand is still much stronger than supply [15–17], particularly in the case of heavy atoms and ions. Accurate interpretation of stellar spectra requires the knowledge not only of oscillator strengths, but also of isotope shifts and hyperfine structures, since they cause an asymmetry and splitting of atomic transitions. Both isotope shift and hyperfine structure are related to the internal properties of the atomic nucleus. The experimentally observable energy shifts and interaction constants can be evaluated as products of the electronic and nuclear factors (as described in section VI). The nuclear properties may therefore be extracted from experimental energy shifts and calculated electronic expectation values. This is particularly useful for determinations of nuclear electric quadrupole moments, which are difficult to measure directly [18].

The whole field of theoretical chemistry originated once from quantum mechanics of many-electron atoms (Dirac [19] expressed this in 1929 as follows: 'The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved') and evolved into a separate branch of science, snowballing on its way in terms of human potential, technical development, and industrial connections. The connections to atomic theory have not been severed, though, since both fields share a good deal of methods, models, and techniques [20–22], and chemical codes frequently exploit atomic theory and atomic data for the purpose of testing or parameterizing their basis sets.

Beyond these immediate connections and applications to basic and applied sciences, one can also envisage several prospects where atomic theory can have potentially important applications. In the emerging fields of single-atom manipulations, controlled chemical dynamics, nanotechnology, atomic-level molecular biology, it is very likely that a strong need can arise for chemical and atomic tools to observe, predict, design, fabricate, modify, and manipulate microscopic objects on an atomic scale. The detailed knowledge of the electronic orbitals of such objects may be equally important as the knowledge of gravity is to manipulate a spaceship in orbit.

## II. ATOMIC MANY-BODY THEORIES

Two years after Schrödinger discovered his equation and applied it successfully to the hydrogen atom, Egil Hylleraas succeeded in performing variational calculation of the energy levels of helium [23], which constituted a proof (or at least strong evidence) that the equation should also correctly describe systems with more than one electron. The techniques developed by Hylleraas are based on the variational function, which is expanded in the basis of functions of the type

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = r_1^{m_1} r_2^{m_2} r_{12}^{m_{12}} \exp(-\alpha_1 r_1 - \alpha_2 r_2) \quad (1)$$

where  $r_1$  and  $r_2$  denote the radial coordinates of the two electrons,  $r_{12}$  is the inter-electronic distance,  $m_1$ ,  $m_2$ ,  $m_{12}$  are integer exponents, and  $\alpha_1$ ,  $\alpha_2$  are variational parameters. Expansions of the form 1 have been found to give increasingly accurate variational eigenvalues as the number of terms increases. Drake [24] succeeded in obtaining solutions for the entire singly-excited spectrum of helium, which are essentially exact for all practical purposes. The Hylleraas expansions have been also applied successfully to lithium and other lithium-like ions [25, 26], but generalization of

this method beyond the three-electron system has proven to be exceedingly difficult.

In the meantime the Rayleigh-Schrödinger perturbation theory [27–29] has been formulated, and over the years evolved into the modern versions, in which diagrammatic [30] and coupled-cluster [31–33] techniques have been employed and applied to variety of problems in atomic physics [34–37]. Another offspring of the perturbational approach is the  $Z$ -expansion theory [38], based on the expansion of the total energy (or any other expectation value) in powers of the atomic number  $Z$

$$E = Z^2 \sum_i E_i Z^{-i}, \quad (2)$$

which is particularly suited for highly ionized systems, where fast convergence of the series is ensured. This approach has also been used extensively, particularly in situations where the behaviour of an atomic property along an isoelectronic series is of interest [39].

A year after the discovery of the Schrödinger equation, Hartree [40] introduced (on purely physical grounds) the idea of a self-consistent field (SCF), and later Fock [41] and Slater [42] made the connection with the variational principle, laying down the foundation for the Hartree-Fock theory, which constitutes the backbone of the present-day multi-electron variational methods (see sections III,IV,V).

### III. HARTREE-FOCK THEORY

Hartree-Fock theory has been presented in a variety of papers (see e.g. [43]) and several books [44–47]. There exist numerous atomic (of which two, by Charlotte Froese Fischer [48] and by Robert D. Cowan [46], dominated the “market”), and countless chemical codes. For the purpose of the present work, it should be emphasized that Hartree-Fock theory constitutes an essentially non-relativistic approximation. The so-called relativistic effects may be included as corrections to the Hamiltonian, most commonly in the Breit-Pauli formulation [49]. It should be mentioned that there is no such thing as the relativistic effect; the term is used as a shorthand to describe the differences between the outcomes of different mathematical models, but it does not correspond to any real physical property, because a ‘non-relativistic’ atom does not exist in nature. These corrections are treated perturbatively, though, which means that they affect only the energy eigenvalues and eigenvector compositions, leaving the radial shapes of one-electron functions unchanged. This approximation works well for light atoms and for the atomic properties whose dependence on the radial form of the wavefunction is weighted towards the outer parts [50]. Some

atomic observables are, however, more sensitive to the form of the calculated electronic wavefunctions close to the nucleus, where direct and indirect effects of relativity [51] are difficult to account for by quasi-relativistic methods. The two prominent examples are the hyperfine structures and the P- and T-violating effects of the weak interaction [11]. The physical picture is that interactions take place either inside or close to the nucleus, which gives rise to contact operators or inverse polynomial factors  $r^{-3}$  in the Hamiltonian (see section VI), which in turn strongly favor electronic orbitals with low angular momenta (predominantly  $s$  and  $p$  symmetries), since their densities are higher in the proximity of the nucleus. The typical distances for the hyperfine interaction are the radii of the innermost shell. In accurate calculations of hyperfine structures it is necessary to take relativistic effects into account even for relatively light elements [52, 53]. The effects of relativity scale as the square of the atomic number  $Z$  and can usually be treated as perturbations for light elements. The effects of electron correlation and relativity are not independent, though. The coupling between them increases with increasing atomic number, and at some point it becomes necessary to employ a fully relativistic approach if accurate results are to be expected [54].

#### IV. DIRAC-HARTREE-FOCK THEORY

The relativistic formulation of atomic many-body theory originates from Quantum Electrodynamics [55–61], through the no-pair Hamiltonian (the term *no-pair* indicates that the effects arising from creation and annihilation of virtual electron-positron pairs are not accounted for [57])

$$H^{\text{no pair}} = \sum_{i=1}^N H_D(r_i) + \sum_{i<j} V(|\vec{r}_i - \vec{r}_j|), \quad (3)$$

where  $H_D$  is the one-electron Dirac operator (atomic units are used throughout; in this units, the velocity of light,  $c$ , has the numerical [62] value  $\alpha^{-1} = 137.035\,999\,074(44)$ , where  $\alpha$  is the fine structure constant)

$$H_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1)c^2 + V(r), \quad (4)$$

where  $V(r)$  is the potential from an extended charge distribution [63].

The  $\boldsymbol{\alpha}$  and  $\beta$  are 4 by 4 matrices, which are usually given in terms of 2 by 2 Pauli matrices  $\sigma_x$ ,  $\sigma_y$ , and  $\sigma_z$

$$\alpha_x = \begin{pmatrix} 0_2 & \sigma_x \\ \sigma_x & 0_2 \end{pmatrix}, \quad \alpha_y = \begin{pmatrix} 0_2 & \sigma_y \\ \sigma_y & 0_2 \end{pmatrix}, \quad \alpha_z = \begin{pmatrix} 0_2 & \sigma_z \\ \sigma_z & 0_2 \end{pmatrix}, \quad \beta = \begin{pmatrix} I_2 & 0_2 \\ 0_2 & -I_2 \end{pmatrix} \quad (5)$$

where  $I_2$  and  $0_2$  are 2 by 2 identity and null matrix, respectively. The last term in equation (3) represents an operator of the electron-electron interaction. The formal theory of QED can in principle yield a perturbation series for full electron-electron interaction [64], but in practice the series has to be truncated and a subset of dominant contributions may be evaluated. When only the interactions arising from one-photon exchange diagram in QED are retained, the operator  $V$  takes the form (in Coulomb gauge):

$$V_{ij} = \frac{1}{r_{ij}} \quad (6)$$

$$- \frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}} \cos\left(\frac{\omega_{ij} r_{ij}}{c}\right) \quad (7)$$

$$- (\boldsymbol{\alpha}_i \cdot \vec{\nabla}_i)(\boldsymbol{\alpha}_j \cdot \vec{\nabla}_j) \frac{\cos(\omega_{ij} r_{ij}/c) - 1}{\omega_{ij}^2 r_{ij}/c^2} \quad (8)$$

where  $r_{ij} = |\vec{r}_i - \vec{r}_j|$  is the inter-electronic distance,  $\omega_{ij}$  is the energy of the photon exchanged between the two electrons,  $\boldsymbol{\alpha}_i$  are the Dirac matrices. The term (6) represents the Coulomb interaction, the second (7) and third (8) involve retardation and magnetic interaction. A series expansion of the operators in (7) and (8) in powers of  $\omega_{ij}/c$  yields the Breit interaction, which includes the leading retardation contribution to the order of  $1/c^2$

$$B_{ij}^R = -\frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{2r_{ij}} - \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})}{2r_{ij}^3}. \quad (9)$$

Apart from the choice of Hamiltonian, there exist also the choice of a trial function to solve the secular equation

$$H | \Psi \rangle = E | \Psi \rangle. \quad (10)$$

The starting point for most of the many-body calculations is the Dirac-Hartree-Fock (DHF) approximation. It is a relativistic equivalent of the Hartree-Fock model, in which electrons are treated in independent-particle approximation, and the one-electron wave functions are evaluated in the Coulomb field of the nucleus and the spherically averaged field of the electrons themselves. This implies that dynamic correlation of motions of the electrons is neglected, except from the exchange correlation. In the relativistic framework electron correlation is then defined as the difference between the binding energy obtained with the full inclusion of the Coulomb interaction and the energy obtained in the Dirac-Hartree-Fock approximation. The definition is sometimes generalized by inclusion of the Breit interaction. The effect of electron correlation on other atomic properties is defined similarly as in the case of the binding energy.

## V. MULTI-CONFIGURATION DIRAC-HARTREE-FOCK THEORY

The relativistic analogue of the Hartree-Fock theory in its early formulations [65–68] was based on the Dirac-Coulomb Hamiltonian

$$H_{DC} = \sum_i c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 - Z/r_i + \sum_{i>j} 1/r_{ij}, \quad (11)$$

in which only the Coulomb part of the electron-electron interaction was retained. The effects of the Breit interaction (along with the leading QED corrections) can be later evaluated perturbatively [69]. The Breit interaction effect on radial wavefunctions becomes important for the orbitals penetrating the proximity of heavy nuclei [70–72], in which case it may become necessary to use the Breit operator beyond the first order perturbation theory [59].

In the standard formulation of the Multi-Configuration Dirac-Hartree-Fock (MCDHF) theory [73], the Atomic State Function (ASF) — the trial function  $\Psi$  in equation (10) — for a state labeled  $\Gamma P J M$  is represented as a linear combination of symmetry-adapted Configuration State Functions (CSF)

$$\Psi(\Gamma P J M) = \sum_r c_r \Phi(\gamma_r P J M). \quad (12)$$

Configuration mixing coefficients  $c_r$  are obtained through diagonalization of the appropriate Hamiltonian. Configuration State Functions  $\Phi(\gamma_r P J M)$ , which are eigenfunctions of the total angular momentum  $J^2$ , its projection  $J_z$ , and inversion operator  $P$  ( $\Gamma$  and  $\gamma$  represent all other quantum numbers necessary to uniquely define an Atomic or a Configuration State Function), are constructed as linear combinations of antisymmetrized products (Slater determinants) of one-electron functions

$$\Phi_S = (n!)^{-1/2} \det | \phi_1(r_1)\phi_2(r_2) \dots \phi_n(r_n) |. \quad (13)$$

In the most commonly employed variant of the Dirac-Hartree-Fock model a Slater determinant is a product of orthonormal one-electron Dirac 4-spinors

$$\phi_i(r) = \phi_{n\kappa m}(r) = \frac{1}{r} \begin{pmatrix} P_{n\kappa}(r)\chi_{\kappa m}(\hat{r}) \\ iQ_{n\kappa}(r)\chi_{-\kappa m}(\hat{r}) \end{pmatrix}, \quad (14)$$

where  $n$  is the principal quantum number, and  $\kappa$  and  $m$  are the relativistic angular quantum number and its  $z$ -component, respectively;  $\kappa = \pm(j + 1/2)$ .  $P_{n\kappa}(r)$  and  $Q_{n\kappa}(r)$  represent the large and small components of the  $i$ -th one-electron radial wavefunction, respectively, and  $\chi_{\kappa m}(\hat{r})$  is the

spinor spherical harmonic in the  $lsj$  coupling scheme

$$\chi_{\kappa m}(\theta, \varphi) = \sum_{m_s} \langle l, m - m_s, \frac{1}{2}, m_s | l, \frac{1}{2}, j, m \rangle Y_{l, m - m_s}(\theta, \varphi) \sigma(m_s), \quad (15)$$

where  $\langle l, m - m_s, \frac{1}{2}, m_s | l, \frac{1}{2}, j, m \rangle$  is a Clebsch-Gordan coefficient, and

$$\sigma(1/2) = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \sigma(-1/2) = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (16)$$

MCDHF equations are obtained by applying the variational principle to the energy functional  $E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$ . Variation with respect to configuration mixing coefficients ( $c_r$  in equation 12) leads to a matrix eigenvalue problem. Variation with respect to the radial wavefunctions leads to a set of integro-differential equations

$$\begin{pmatrix} V_i(r) & -d/dr + \kappa_i/r \\ d/dr + \kappa_i/r & V_i(r) - 2c \end{pmatrix} \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} = \epsilon_{ii} \begin{pmatrix} P_i(r) \\ Q_i(r) \end{pmatrix} + \begin{pmatrix} \chi_i^P(r) \\ \chi_i^Q(r) \end{pmatrix} + \sum_{j \neq i} \epsilon_{ji} \begin{pmatrix} P_j(r) \\ Q_j(r) \end{pmatrix}, \quad (17)$$

where  $V_i$  represents the sum of the nuclear potential and direct part of the electron-electron potential,  $\chi_i^P$  and  $\chi_i^Q$  represent exchange potentials for the large and small components, respectively,  $\epsilon_{ii}$  is the diagonal Lagrange parameter introduced to enforce normalization,  $\epsilon_{ij}$  is the off-diagonal Lagrange parameter introduced to enforce orthogonality between orbitals with the same spherical symmetry (i.e. identical values of  $\kappa$ ) and different values of the principal quantum number

$$\int_0^\infty dr (P_{n\kappa}(r)P_{m\kappa}(r) + Q_{n\kappa}(r)Q_{m\kappa}(r)) = \delta_{nm}. \quad (18)$$

The equations (17) are solved numerically, which requires that the radial functions  $P_{n\kappa}$  and  $Q_{n\kappa}$  are expanded on a spatial grid or in a suitably chosen basis of analytic functions (see references [74, 75] for details). The numerical algorithms to solve the equations (17) have been described in several papers [66, 73], as well as in the published manuals of the computer codes [63, 67, 68, 76]. qqq Several hundred research papers appear each year in the loosely-defined field of the 'relativistic theory of atoms and molecules' [77–79]. The calculations described in the references [80–97] and in the present work were performed with the use of GRASP code [98, 99], which was extended to accommodate very large configuration expansions [76, 100] and supplemented with a new configuration space generator [101]. In addition, recent developments on

the RATIP program [102, 103] help perform detailed MCDF computations for a large number of ionization and recombination properties that are affected also by electrons in the continuum.

## VI. HYPERFINE INTERACTION

The hyperfine structure of atomic energy levels is caused by the interaction between the electrons and the electromagnetic multipole moments of the nucleus. The effects of the hyperfine interaction are usually small in comparison with the fine structure, and they may almost always be analyzed in first-order perturbation theory [104–106]. In some cases off-diagonal matrix elements yield measurable corrections to the first-order structures [107], or induce effects, which otherwise would be forbidden (e.g. hyperfine-induced transitions [108, 109]). The study of hyperfine structures in atoms, molecules, and solids has theoretical or practical implications in atomic, chemical, and solid-state spectroscopy, astrophysics, plasma physics, nuclear physics, nuclear magnetic resonance, nuclear quadrupole resonance, electron-nuclear double resonance, Mössbauer spectroscopy, technology of polarized beams, nuclear orientation, and several other methods and techniques (see reference [10] for a general overview of hyperfine interaction; experimental techniques were recently reviewed by Svanberg [110]).

The hyperfine contribution to the Hamiltonian can be represented by a multipole expansion [111]

$$H_{\text{hfs}} = \sum_{k \geq 1} \mathbf{T}^{(k)} \cdot \mathbf{M}^{(k)}, \quad (19)$$

where  $\mathbf{T}^{(k)}$  and  $\mathbf{M}^{(k)}$  are spherical tensor operators of rank  $k$  in the electronic and nuclear space, respectively [105]. The lowest  $k = 0$  term may be used to evaluate the effects of finite volume of nuclear charge, which contribute to the isotope shifts, i.e. the differences in energy levels between different isotopes of the same element. These effects are outside the scope of the present work, though. The  $k = 1$  term represents the magnetic dipole interaction and the  $k = 2$  term the electric quadrupole interaction. Higher order terms are much smaller (magnetic octupole shifts are typically  $10^8$  times smaller than magnetic dipole [112]), difficult to measure, and are usually neglected.

The electronic tensor operators are sums of one-particle tensor operators

$$\mathbf{T}^{(k)} = \sum_{i=1}^N \mathbf{t}_i^{(k)}, \quad k = 1, 2, \dots \quad (20)$$

The magnetic dipole operator  $\mathbf{t}^{(1)}$  in the non-relativistic framework takes the form [105]

$$\mathbf{t}_i^{(1)} = \frac{\alpha^2}{2} \{2 \mathbf{l}_i^{(1)} r_i^{-3} + g_s \frac{8}{3} \pi \delta(\mathbf{r}_i) \mathbf{s}_i^{(1)} - g_s \sqrt{10} [\mathbf{C}^{(2)}(i) \times \mathbf{s}_i^{(1)}]^{(1)} r_i^{-3}\}. \quad (21)$$

where  $g_s$  is the electronic  $g$ -factor. The three terms in the equation (21) are usually called *orbital*, *Fermi-contact*, and *spin-dipole* term, respectively. The magnetic dipole operator  $\mathbf{t}^{(1)}$  in the relativistic framework has the form [105]

$$\mathbf{t}_i^{(1)} = -i\alpha \boldsymbol{\alpha}_i \cdot \mathbf{l}_i \mathbf{C}^{(1)}(i) r_i^{-2}. \quad (22)$$

The electric quadrupole term has the form

$$\mathbf{t}_i^{(2)} = -\mathbf{C}^{(2)}(i) r_i^{-3}. \quad (23)$$

In the formulas above  $\alpha$  is the fine-structure constant,  $\boldsymbol{\alpha}$  is the vector of the three Dirac matrices (see eq. 5), and  $\mathbf{C}^{(k)}$  is a spherical tensor with the components related to the spherical harmonics as

$$C_q^{(k)} = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}. \quad (24)$$

The magnetic dipole operator (eq. 22) represents the magnetic field generated by the electrons at the site of the nucleus. The electric quadrupole operator (eq. 23) represents the electric field gradient at the nucleus. The nuclear magnetic dipole moment  $\mu_I$  and nuclear electric quadrupole moment  $Q$  are defined through the expectation values of the nuclear tensor operators  $\mathbf{M}^{(1)}$  and  $\mathbf{M}^{(2)}$  in the state with the maximum component of the nuclear spin,  $M_I = I$ :

$$\langle \gamma_{III} | \mathbf{M}_0^{(1)} | \gamma_{III} \rangle = \mu_I, \quad (25)$$

$$\langle \gamma_{III} | \mathbf{M}_0^{(2)} | \gamma_{III} \rangle = \frac{Q}{2}. \quad (26)$$

The hyperfine interaction quantizes the orientation of the nuclear spin  $\mathbf{I}$  with respect to the electromagnetic field generated at the site of the nucleus by the orbital and spin motions of the electrons. In terms of angular theory, the hyperfine interaction couples the electronic and nuclear angular momenta to a total angular momentum

$$\mathbf{F} = \mathbf{I} + \mathbf{J}. \quad (27)$$

The eigenstates of the system are then represented by the eigenfunctions of the resulting total angular momentum  $\mathbf{F}$

$$\psi = |\gamma_I \gamma_J I J F M_F \rangle, \quad (28)$$

where  $\gamma_I$  and  $\gamma_J$  represent the remaining quantum numbers necessary to specify the state completely. In this representation, perturbation theory gives the following hyperfine corrections to the electronic energy

$$\Delta E_{M1} = \langle \gamma_I \gamma_J I J F M_F | \mathbf{T}^{(1)} \cdot \mathbf{M}^{(1)} | \gamma_I \gamma_J I J F M_F \rangle, \quad (29)$$

$$\Delta E_{E2} = \langle \gamma_I \gamma_J I J F M_F | \mathbf{T}^{(2)} \cdot \mathbf{M}^{(2)} | \gamma_I \gamma_J I J F M_F \rangle. \quad (30)$$

Using the Wigner-Eckart theorem [46],

$$\langle \gamma J M | T_Q^{(K)} | \gamma' J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & K & J' \\ -M & Q & M' \end{pmatrix} \langle \gamma J || \mathbf{T}^{(K)} || \gamma' J' \rangle, \quad (31)$$

these can also be written as

$$\Delta E_{M1} = (-1)^{I+J-F} W(IJ IJ; F1) \langle \gamma_J J || \mathbf{T}^{(1)} || \gamma_J J \rangle \langle \gamma_I I || \mathbf{M}^{(1)} || \gamma_I I \rangle, \quad (32)$$

$$\Delta E_{E2} = (-1)^{I+J-F} W(IJ IJ; F2) \langle \gamma_J J || \mathbf{T}^{(2)} || \gamma_J J \rangle \langle \gamma_I I || \mathbf{M}^{(2)} || \gamma_I I \rangle, \quad (33)$$

where  $W(IJ IJ; F1)$  and  $W(IJ IJ; F2)$  are  $W$  coefficients of Racah [46].

Energies are usually expressed in terms of the hyperfine interaction constants  $A$  and  $B$ :

$$A = \frac{\mu_I}{I} \frac{1}{[J(J+1)(2J+1)]^{\frac{1}{2}}} \langle \gamma_J J || \mathbf{T}^{(1)} || \gamma_J J \rangle, \quad (34)$$

$$B = 2Q \left[ \frac{2J(2J-1)}{(2J+1)(2J+2)(2J+3)} \right]^{\frac{1}{2}} \langle \gamma_J J || \mathbf{T}^{(2)} || \gamma_J J \rangle \quad (35)$$

in which nuclear factors are represented by  $\mu_I$  and  $Q$ , as defined in equations (25) and (26). The energy corrections are then given by

$$\Delta E_{M1} = \frac{1}{2} A_J C, \quad (36)$$

$$\Delta E_{E2} = B_J \frac{\frac{3}{4} C(C+1) - I(I+1)J(J+1)}{2I(2I-1)J(2J-1)}, \quad (37)$$

where  $C = F(F+1) - J(J+1) - I(I+1)$ .

When the Atomic State Function is expanded in terms of Configuration State Functions, the hyperfine interaction constants  $A$  and  $B$  are given by

$$A = \frac{\mu_I}{I} \frac{1}{[J(J+1)(2J+1)]^{1/2}} \sum_{r,s} c_r c_s \langle \gamma_r J || \mathbf{T}^{(1)} || \gamma_s J \rangle, \quad (38)$$

and

$$B = 2Q \left[ \frac{2J(2J-1)}{(2J+1)(2J+2)(2J+3)} \right]^{\frac{1}{2}} \sum_{r,s} c_r c_s \langle \gamma_r J \| \mathbf{T}^{(2)} \| \gamma_s J \rangle. \quad (39)$$

The matrix element  $\langle \gamma_r J \| \mathbf{T}^{(k)} \| \gamma_s J \rangle$  between  $jj$ -coupled Configuration State Functions involves only one-particle tensor operators (eq. 20) and it can be decomposed [99, 113] into terms that involve single-particle orbitals only

$$\langle \gamma_r J \| \mathbf{T}^{(k)} \| \gamma_s J \rangle = \sum_{a,b} d_{ab}^k(rs) \langle n_a \kappa_a \| \mathbf{t}^{(k)} \| n_b \kappa_b \rangle. \quad (40)$$

The single-particle matrix elements reduce to an angular factor and a radial integral

$$\langle n_a \kappa_a \| \mathbf{t}^{(1)} \| n_b \kappa_b \rangle = -\alpha(\kappa_a + \kappa_b) \langle -\kappa_a \| \mathbf{C}^{(1)} \| \kappa_b \rangle \langle r^{-2} \rangle_{n_a \kappa_a n_b \kappa_b}^M, \quad (41)$$

$$\langle n_a \kappa_a \| \mathbf{t}^{(2)} \| n_b \kappa_b \rangle = -\langle \kappa_a \| \mathbf{C}^{(2)} \| \kappa_b \rangle \langle r^{-3} \rangle_{n_a \kappa_a n_b \kappa_b}^E. \quad (42)$$

The reduced angular matrix elements are given by

$$\langle \kappa \| \mathbf{C}^{(k)} \| \kappa' \rangle = (-1)^{j+1/2} \sqrt{(2j+1)(2j'+1)} \begin{pmatrix} j & k & j' \\ 1/2 & 0 & -1/2 \end{pmatrix} \pi(l, k, l'), \quad (43)$$

$$\pi(l, k, l') = \begin{cases} 1, & \text{if } l + k + l' \text{ even} \\ 0, & \text{otherwise} \end{cases} \quad (44)$$

and the radial integrals by

$$\langle r^{-2} \rangle_{n\kappa n'\kappa'}^M = \int r^{-2} (P_{n\kappa}(r) Q_{n'\kappa'}(r) + Q_{n\kappa}(r) P_{n'\kappa'}(r)) dr, \quad (45)$$

and

$$\langle r^{-3} \rangle_{n\kappa n'\kappa'}^E = \int r^{-3} (P_{n\kappa}(r) P_{n'\kappa'}(r) + Q_{n\kappa}(r) Q_{n'\kappa'}(r)) dr. \quad (46)$$

Equations (38) and (39) relate nuclear properties (nuclear magnetic dipole moment  $\mu_I$  and nuclear electric quadrupole moment  $Q$ ), experimentally observable hyperfine constants  $A$  and  $B$ , and the properties of the electronic cloud (eqs. 22 and 23), which can be calculated according to the procedure outlined above. While nuclear dipole magnetic moments can be measured very accurately (the most comprehensive tabulation can be found in references [114, 115]), nuclear electric quadrupole moments are very difficult to measure by direct nuclear techniques [106, 116], and currently the best way to determine them is a combination of atomic or molecular theory with experiment [18] in which calculated electric field gradients, together with experimental values of

hyperfine constant  $B$ , are used to extract the nuclear electric quadrupole moment  $Q$ , by using equation (39), which can be simplified to

$$B(\Gamma P J) = Q \cdot EFG(\Gamma P J), \quad (47)$$

where  $EFG(\gamma P J M)$  denotes the electric field gradient for a particular atomic state, and  $Q$  is the electric quadrupole moment of the nucleus.

## VII. COMPLETE ACTIVE SPACE

The term Active Space originates from theoretical chemistry [117, 118], where it is associated with expansion of quantum-mechanical function of a molecule in terms of (usually analytical, and most often built from Gaussian functions) orbital basis sets. Complete Active Space (CAS) within a given basis set means by definition the wavefunction built from all Configurations State Functions which can be generated by substitutions from a reference configuration (or configurations) to a set of active orbitals. The adjective 'active' refers to those one-electron orbitals which actively participate in electron substitutions. In atomic theory the meaning of the CAS term is usually (although not universally) extended to denote not only the saturation of the configurational space within the given orbital set (i.e. no restrictions on electron substitutions within the orbital set), but also the saturation of the orbital space itself, usually by a systematic (i.e. stepwise) increase of the orbital space [53, 119, 120]. In both cases the saturation is understood in the context of a functional dependence of a specific atomic (or chemical) property on the size of the orbital or configurational space. In this sense the saturation of the space is equivalent to the saturation of that property with respect to the appropriately defined size of the configurational or orbital space which leads to the so called "MCHF limit". Both concepts can be illustrated by inspection of the Table I of reference [80], where the hyperfine magnetic dipole hyperfine constant  $S$  of the ground state of lithium is presented as a function of the orbital set (first column) and of the size of configuration set (third column). Each of the first six rows of the Table I corresponds to a Complete Active Space calculation within a given orbital set. Term "SDT" indicates 'single and double and triple' substitutions (i.e. all these electrons are subject to substitutions within the full orbital set). In the subsequent rows only single and double (SD) substitutions were permitted, but the effects of the omitted triple substitutions were later recovered in Configuration-Interaction (CI) calculations. Successive increase of the orbital set leads to the saturation of the expectation value of  $A$  against

the size of the orbital space, as can be seen in the Figure I of reference [80].

An analogous calculation for the lithium-like  $\text{Be}^+$  ion is presented in the figures FIG.1 and FIG.2 of the present paper (both these figures are based on the calculations performed in the reference [81]). The figure FIG.1 shows the full graph, which demonstrates the considerable contribution, of the order of 20%, of the  $3s$  orbital to the magnetic dipole constant  $A$  of the  $1s^2 2s^2 S_{1/2}$  state of  ${}^9_4\text{Be}^+$ . The contributions of the subsequent electronic shells decrease rapidly, as can be seen in the figure FIG.2, but fifteen orbital layers were necessary to saturate the expectation value of  $A$ . The error bar attached to the last point on the curve shows the estimated accuracy of the calculated hyperfine constant  $A({}^9_4\text{Be}^+) = -625.04(8)$  MHz. The dominant contribution to the theoretical error bar is the uncertainty of the magnetisation distribution inside the nucleus (Bohr-Weisskopf effect [121]). The calculated  $A$  value should be compared to the experimental result  $A({}^9_4\text{Be}^+) = -625.008\,837\,048(10)$  MHz [122], which is represented by a blue cross in the figure FIG.2. The size of the cross does not reflect the experimental error bar, which is negligibly small compared to the theoretical uncertainty. Both the abovementioned calculations illustrate the fact, that very large multiconfiguration expansions are necessary to saturate the electron correlation effects.

## VIII. COMPLETE ACTIVE SPACE FOR LIGHT SYSTEMS

The concept of the Active Space has been used extensively in the non-relativistic atomic theory in various applications [43, 123–125]. In particular, the properties of lithium and lithium-like systems were subject of several papers, since lithium constitutes the first truly multi-electron system, due to the existence of two spatially separated electron shells. Among other properties, multi-configuration Hartree-Fock calculations provided very accurate values of hyperfine constants of several levels of neutral lithium [50, 126, 127] (some of which were more accurate (and in disagreement with) experimental results — see reference [127]), as well as resonance transition rate [128], which contradicted the experimental value [129], while being in perfect agreement with several other theoretical methods (the contradiction was later resolved [130] in favor of the theory).

The research into the electron-correlation effects within the fully relativistic Dirac-Hartree-Fock model has nearly as long history [22], but all early efforts were hampered by technological shortcomings (primarily by the insufficient computer memory capacities and algorithmic instabil-

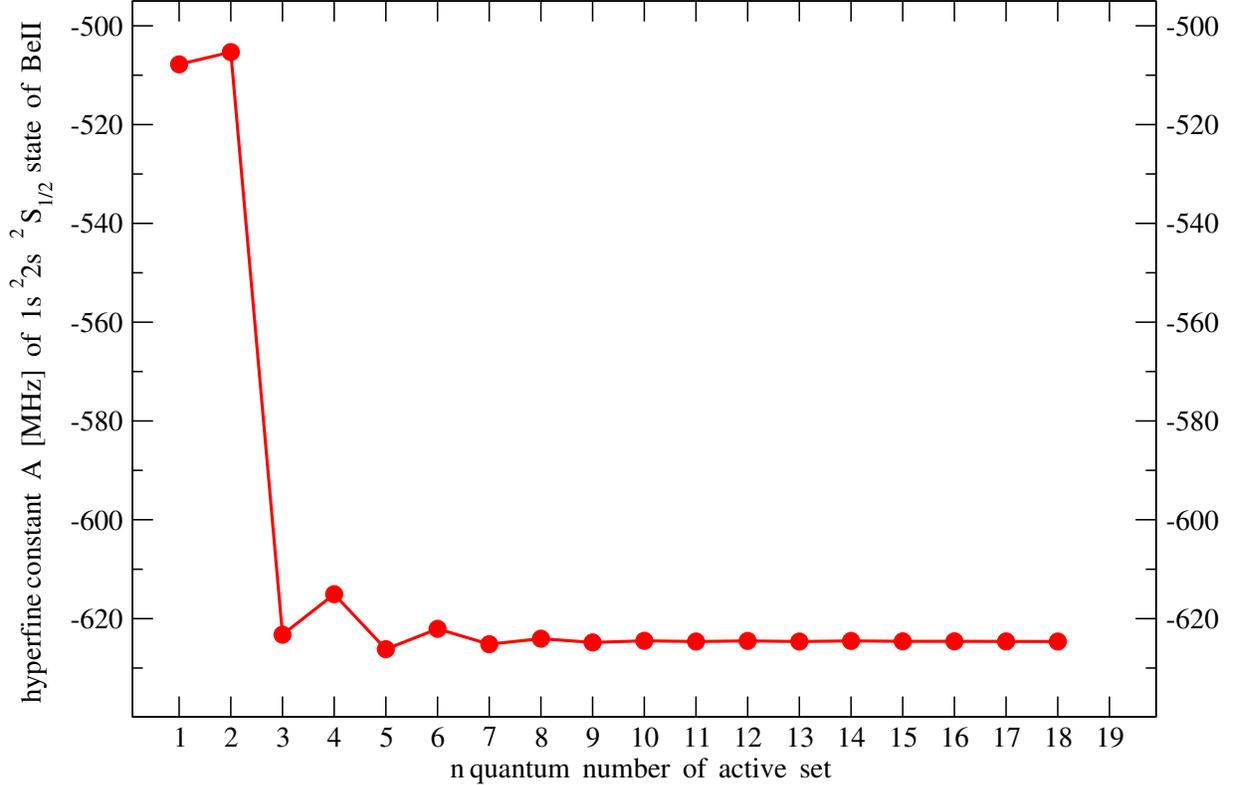


FIG. 1: (Color online): Magnetic dipole constant (in MHz) for the  $1s^2 2s^2 S_{1/2}$  state of  ${}^9\text{Be}^+$  as a function of orbital set.

ities of the computer codes) and the selection of the multi-configuration spaces was all too often based on the art of educated guessing and intuition [131]. The first large-scale relativistic calculations became feasible when tools and techniques developed by the Vanderbilt group [132] were implemented into the Oxford MCDHF code GRASP [63, 68]. The resulting package [76, 98, 100], together with the accompanying modules for hyperfine expectation values [99] and configuration-space generator [101], permitted systematic studies of electron-correlation effects within the Dirac-Hartree-Fock model [133], which brings us to the subject of the present work.

References [80, 81] constitute the first applications of the CAS-MCDHF model in atomic theory. In both cases the systems under study were very light (i.e. non-relativistic) and testing was the sole purpose of the calculations. Hyperfine interaction was chosen as testing ground, because it is sensitive to both relativistic and correlation effects, very accurate experimental values of magnetic dipole constants exist for many systems, and comparisons with several other theoretical models are possible. In both cases an attempt was made to extrapolate the systematic expansions of the active set, so as to achieve the level of approximation which might be called an MCDHF limit,

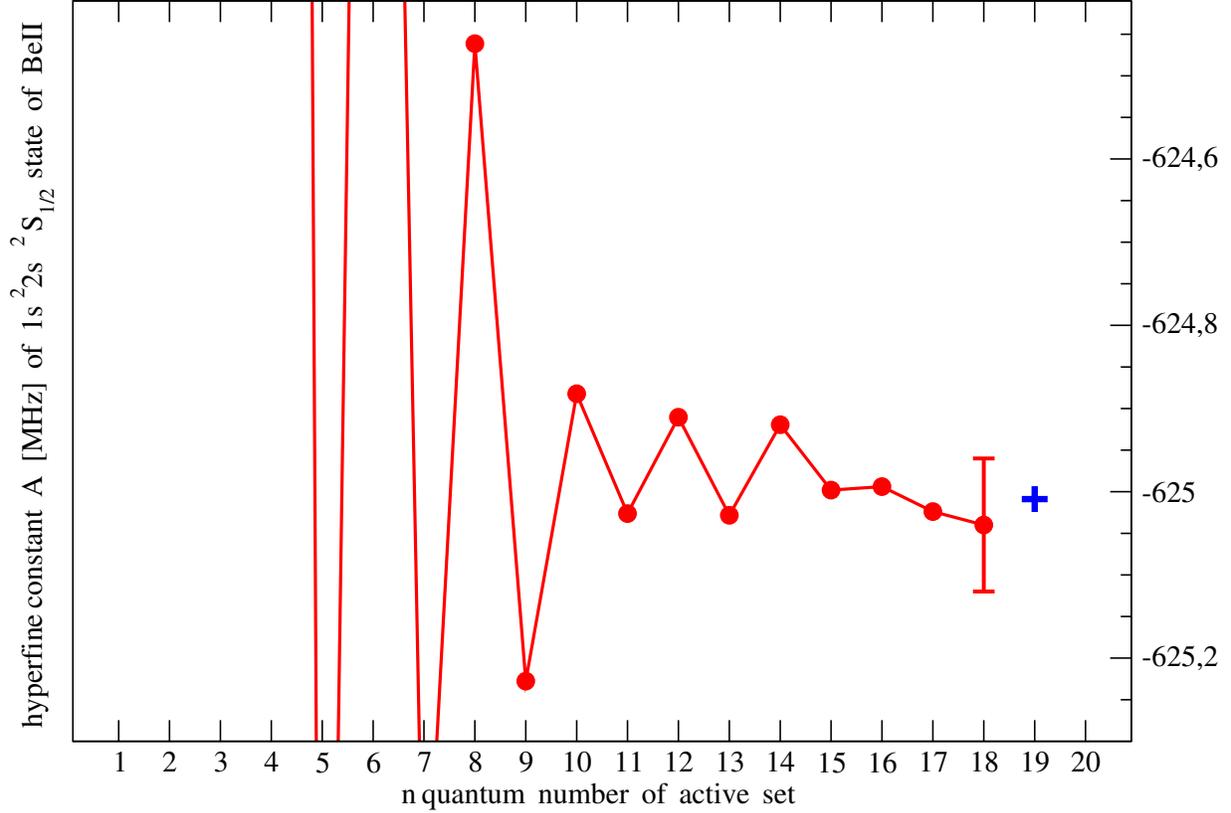


FIG. 2: (Color online): Magnetic dipole constant (in MHz) for the  $1s^2 2s^2 S_{1/2}$  state of  ${}^9\text{Be}^+$  as a function of orbital set. The figure shows the blown-up tail portion of the full graph, corresponding to these orbital sets, for which principal quantum number of virtual orbitals is allowed to exceed 7.

bearing in mind that this concept is somewhat more fuzzy than its non-relativistic counterpart, and perhaps a “no-pair” MCDHF limit (see section IV) would be a better description. Within the limitations of the model (among several factors, the distribution of electromagnetic moments inside the nucleus (Bohr-Weisskopf effect [121]) constitutes the primary limitation of the accuracy of the calculations of atomic hyperfine structures; they have drawn much attention in recent years — see references [134–142] — but the fact is that these distributions are generally unknown) and bearing in mind that within the domain of light, neutral atoms non-relativistic methods have several advantages over fully relativistic Dirac-Hartree-Fock methods, the values obtained in papers [80] and [81] are nearly as accurate as the results obtained within the semi-relativistic Hartree-Fock [126] and Hylleraas models [25].

## IX. RESTRICTED ACTIVE SPACE FOR HEAVY SYSTEMS

The straightforward, orthodox approach of CAS appears to be feasible only in the cases of atomic systems with very limited number of electrons, because the size of the CSF space increases factorially with the number of spinors. Otherwise restrictions have to be imposed on the configuration-space generator. The most common type of such restriction is a limitation of the number of active electrons, i.e. the electrons which are subject to substitutions from reference configuration(s) to the active space. As mentioned in section VII, Table I of reference [80] provides an example of the restriction where (beginning from the seventh row) the number of active electrons has been limited to 2 (as indicated by “SD” entry in column 2). Apart from the limitation of the number of active electrons, the restrictions may also be imposed on the electron occupations of one-electron orbital shells. The concept of the Restricted Active Space [118] is frequently utilized in the context where the total orbital space is partitioned into several subspaces, each of them subjected to limitations of the number of electrons which may populate a particular subshell. In the most simple implementation, the orbital space is divided into inactive (usually closed core shells), valence, and virtual (i.e. those which are empty in reference configuration) spaces (see references [87, 118] for more details).

Reference [82] provides an example of calculation where the number of active electrons has been limited to one, while permitting substitutions from all core orbitals. This approximation (which might be called ‘CAS-singles’) works very well in calculations of hyperfine structures, when Atomic State Function of a particular level is to a good approximation described by one Configuration State Function, i. e. there is one clearly dominating mixing coefficient  $c_r$  (see eq. 12), because single substitutions comprise the dominant part of the hyperfine energy correction, due to the fact that the hyperfine energy operators (eq. 20) are one-body operators, and therefore in the first-order perturbation theory only single substitutions contribute to the hyperfine energy operator [106, 143]. This observation was the basis of the series of papers [83–86, 88–92] in which nuclear quadrupole moments of several isotopes were determined by a semi-empirical method, described near the end of the section VI, combined with a statistical averaging over several electronic levels of a system (see references [83, 85] for details). Apart from the accurate calculation of hyperfine constants and splitting, MCDF computations in a moderate basis demonstrated an unexpected large hyperfine-induced modification in the  $K\alpha_1$  angular distributions of highly-charged ions [144, 145].

## X. TOWARDS COMPLETE ACTIVE SPACE MODEL FOR HEAVY ATOMS

The basic limitation of the ‘CAS-singles’ approach, described in the previous section, is the omission of higher-order substitutions. In the particular case of the hyperfine interaction, higher-order substitutions do not directly enter the hyperfine operators, but their effects come indirectly through the rearrangement of the Atomic State Function composition (eq. 12). In the ‘CAS-singles’ expansion the configuration mixing coefficients  $c_r$  may be regarded as components of an ASF vector, spanning a particular multi-configuration subspace of the total Hilbert space. The ‘singles’ subspace is built from all Configuration State Functions which can be constructed from the reference state by single substitutions. When double (or higher) substitutions are permitted, the ASF vector spans a larger ‘singles-and-doubles’ (or still larger) subspace, and its components are not necessarily the same as they were in the ‘singles’ subspace, thus affecting the hyperfine expectation values (see eqs. 38 and 39). The operators representing the electron-electron interaction (6) are two-body operators, therefore double substitutions play a dominant role in electron-correlation calculations. The effects of double substitutions on the hyperfine constants of very heavy elements were studied in papers [87, 88, 93–95]. The basic strategy is to split correlation effects into two (or more) categories, corresponding to ‘single’ and ‘double’ (and still higher) substitutions. The orbital space is then generated in ‘single-substitution’ approximation, which usually captures dominant part of the electron-correlation effects (these effects being understood in the context of the hyperfine expectation values). The correlation effects arising from the double substitutions are later evaluated in Configuration Interaction calculations (i.e. without any changes to the orbital space). The saturation of hyperfine expectation values is achieved in a two-step process (see Tables III and VI of reference [87]). In the first step the ‘single-substitution’ space is systematically expanded, until the convergence of the expectation values is obtained. In the second step the procedure of the systematic expansion is repeated within the ‘double-substitution’ space (built from the same spinors, which were generated in the previous step). When double substitutions are permitted in the configuration space generator, the size of the multi-configuration expansion grows too rapidly to allow all of them to span full orbital space. In such a situation the second step may be further divided into sub-steps, and substitutions from particular valence and core shells may be sequentially driven to saturation in virtual orbital space (an example is given in paper [88]). In principle, this procedure could be continued with higher-order substitutions, but the sizes of the multi-configuration expansions quickly outgrow memory capacities of currently available com-

puters. A more elaborate approach to the virtual orbital space has been developed in the recent papers [93–95]. The virtual orbitals were generated with single and restricted double substitutions (SrD) from valence and core orbitals. The restriction was applied to double substitutions in such a way that only one electron was substituted from core shells, the other one had to be substituted from valence shells. The Figure 3 of the reference [94] presents the process of the saturation of the expectation values obtained from the calculations carried out in three different approximations. The reader is referred to the paper [94] for more details.

Different possible approaches to generation of the virtual orbital space are presented in the figure FIG.3 of the present paper (the figure is based on the reference [95]). The three pairs of differently marked and colored curves represent the results of the calculations of magnetic field ( $A/g$ ) and electric field gradient ( $EFG$ ) for the  $5p^2P_3/2$  state of  $\text{Cd}^+$  ion. The curve with rectangles (green online) represents the calculations, where all single and unrestricted double (SrD) substitutions were allowed from valence and core orbitals to the virtual orbital set. The virtual orbital set was systematically increased, up to the largest set, in which the largest principal quantum number  $n$  was set to 6. The curve with circles (magenta online) represents the calculations, where single and restricted double (SrD) substitutions (restrictions as described above) were allowed from valence and core orbitals to the virtual orbital set, up to the largest set, where the principal quantum number  $n$  was set to 10. The curve with diamonds (blue online) represents calculations, where only single (S) substitutions were allowed from valence and core orbitals to the virtual orbital set, up to the principal quantum number  $n = 7$ . The three pairs of curves illustrate the convergence (or lack thereof) of different methods and, even more importantly, they show the discrepancies between the methods themselves. Each method targeted different electron correlation effects, and each of the series of the calculations was based on a specific, limited set of electronic configurations, therefore the three curves converged to slightly different limits. The errors introduced by omitted configurations can be estimated either with the procedure described in reference [81], the statistical approach [83, 85], or with the methods developed in the papers [87, 88, 94]. It can be shown by straightforward algebra (see e.g. reference [105]) that for bound states the integrals on the right-hand sides of equations (45) and (46) are both approximately proportional to the expectation value  $\langle r^{-3} \rangle$ . Therefore the experimental value of the magnetic dipole hyperfine constant  $A$  (which usually can be accurately measured) may be used to estimate the precision of the calculation of the electric quadrupole moment, as described in [88]. Combined with sufficiently accurate experimental values of the electric quadrupole hyperfine moment  $B$  (which have been measured

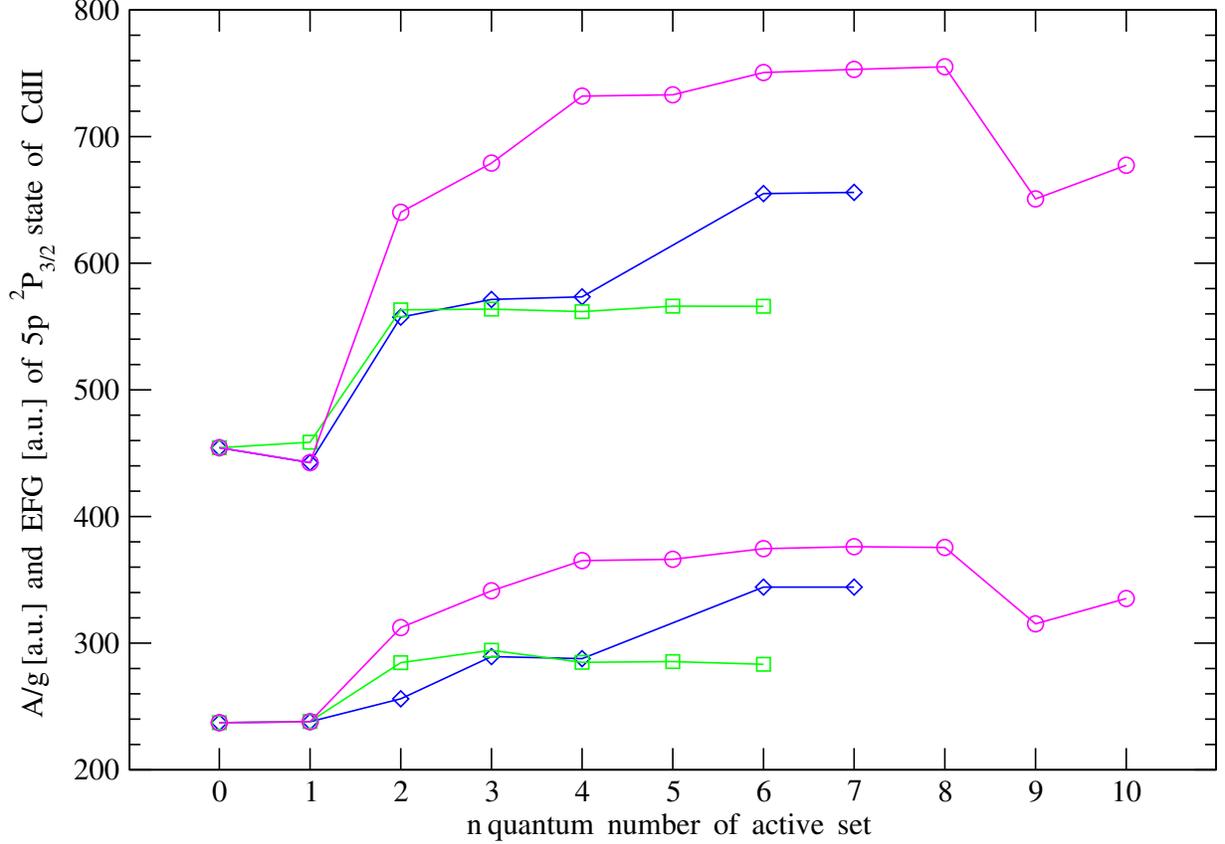


FIG. 3: (Color online): Magnetic field ( $A/g$ ) (lower 3 curves) and electric field gradient  $EFG$  (upper 3 curves), all in atomic units, for the  $5p^2P_{3/2}$  state of  $Cd^+$  ion, as a function of the size of the virtual orbital set. The curve with rectangles (green online) represents calculations with single and unrestricted double (SD) substitutions; the curve with circles (magenta online) represents calculations with single and restricted double (SrD) substitutions; the curve with diamonds (blue online) represents calculations with single only (S) substitutions.

for the ground states of many elements) this method appears to be the best tool for the determination of nuclear quadrupole moments for heavy elements. Similar sizable and restricted orbital spaces have been applied recently to calculate the isotope shift (IS) parameters for several medium and heavy elements [146, 147]. These IS parameters describe the electronic response that is needed to separate the nuclear parameter, such as nuclear spins and changes in the nuclear radius, from the observed transition frequencies. For a long time, these laser-spectroscopic measurements of optical isotope shifts have formed a major probe of such radii and have the advantage that the nuclear parameters can be determined (almost) independently of any nuclear model [148].

## Conclusions

The algebraic formulation of classical mechanics was put forward by Isaac Newton in the second half of the seventeenth century and published, in his *Philosophiae Naturalis Principia Mathematica*, in 1687. Over the next two centuries Lagrangian and Hamiltonian techniques to the point where a variety of many-body problems could be solved to very high accuracy. The twentieth century advanced at somewhat faster pace [149], but three quarters after the discovery of quantum mechanics the algebraic methods and computational tools still do not permit the determination of even the most basic properties of some lanthanide and actinide elements [150]. The many-body problem in the domain of classical mechanics does not have analytic solutions either, but there exist tools and algorithms [151] which permit sending a spaceship to the Moon or to a comet [152], bringing it back to Earth, and landing it on the Pacific within a few hundred meters from the receiving party [153]. Viewed as a transition of (macroscopic) body, it can be calculated and performed with relative accuracy of the order of  $10^{-9}$ . On the other hand, the rate of the lithium or sodium resonance transition (these are the two of the most often visited atomic transitions) can be calculated or measured with at most  $10^{-3}$  accuracy [130]. This is obviously a somewhat misleading comparison, but it gives a perspective from which atomic and molecular many-body theories may be viewed.

It is generally accepted that perturbational many-body theories are formally more rigorous and provide more stable algorithms for the determination of atomic properties than variational theories. On the other hand, Hartree-Fock and Dirac-Hartree-Fock methods are more general, faster, and easier to use for open-shell systems, so in the foreseeable future they are unlikely to be superseded, except perhaps for closed-shell or alkali-like elements [154]. In the present work an overview has been given on the current status of the Dirac-Hartree-Fock theory. The following may be regarded as the most important results of the research presented in the references [80–97]:

- Development of the Complete Active Space model within the Dirac-Hartree-Fock theory. Systematic calculations of atomic properties in fully relativistic approach with full account of electron correlation made possible.
- The first calculations of atomic properties with the use of the CAS-MCDHF model, yielding accurate results (for light elements the method converges to semi-relativistic models).
- Calculations of hyperfine structures within CAS-MCDHF and more restricted models.

- Currently the most accurate method of determination of nuclear electric quadrupole moments for heavy elements, which combines experimental values of electric quadrupole constants  $B$  with theoretical electric field gradients EFG. The method employs the experimental and calculated magnetic dipole hyperfine constants  $A$  to estimate accuracy of nuclear electric quadrupole moments.
- Statistical method of determination of nuclear electric quadrupole moments.
- Calculations of nuclear electric quadrupole moments for several elements.
- Calculations of electric dipole moments, resulting from  $(P, T)$ -odd interactions of bound electrons with nuclear electromagnetic moments leading to violations of discrete symmetries.

Beside of various bound-state energies and properties, much emphasis has been placed in recent years to describe also photo and autoionization processes of atoms as well as the electron capture into multiply-charged ions. For these processes with one electron in the continuum, the (multiconfiguration) Dirac-Hartree Fock theory has been found very versatile and often superior to many-body perturbation approaches; it has been implemented for example within the RATIP code [103] and supports the computation of nonradiative (electron emission and capture) rates, relative Auger intensities and angular distribution parameters. The RATIP program has been widely used for studying electron emission processes after inner-shell excitation [155] and the ionization of atoms [156] as well as for analyzing the coherence transfer through Auger cascades [157, 158]. In particular, if the fine-structure splitting is small or comparable to the natural line widths of the levels, the angular emission of the (second-step) Auger electrons can be strongly modified due to the *coherent* decay in the cascade [159].

In addition, the RATIP program has been employed for studying the interference of direct and resonant photoionization channels in atomic argon [160] as well as for analyzing the sequential two-photon double ionization of various noble gases in intense free-electron laser (FEL) radiation [161, 162].

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