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Many-body multiconfigurational Dirac-Fock calculation of hyperfine interaction in $7s$, $7p_{1/2}$, and $7p_{3/2}$ states of Ra II

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The techniques of relativistic many-body calculations on atoms and ions have been used to reformulate the multiconfigurational Dirac-Fock techniques in such a way that good wave functions can be obtained with the same accuracy as with many-body perturbation theory, and a relationship between both approaches has been established. As an example the hyperfine interactions of the $7s$, $7p_{1/2}$, and $7p_{3/2}$ states of Ra^+ have been successfully calculated and are in good agreement with experiment.

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INTRODUCTION

The first-principles calculation of atomic hyperfine interactions (hfi) is still a great challenge for atomic theorists. It provides an excellent test of the usefulness of physical and numerical models with which the wave functions, required for obtaining the hfi constants, are calculated. Accurate wave functions are of great importance for the growing need to predict various physical properties of atomic systems either isolated or in a solid-state environment. During the past two decades the methods for obtaining the wave functions and the numerical codes required have been developed to such a high level that accurate wave functions can be obtained for a large class of atomic systems, particularly those with one electron outside closed shells. There have been many publications in this field of which some of the leading ones are given in Refs. [1–8]. We will here only indicate some points important for the introduction to our approach. The main breakthrough in the field has been the introduction of many-body analysis and techniques, similar to those of Feynman in his famous work on quantum electrodynamics. This means a systematic perturbation expansion is taken to represent the wave function we are looking for. Lindgren and Morrison [9] give in their book many details of the approach in nonrelativistic formalism. The major successes, however, were in relativistic theory. Even for light systems like calcium the relativistic modification to, for instance, hyperfine interaction is as large as 4% [10]. The relativistic approach has some additional problems to those mentioned in the book of Lindgren and Morrison. A good idea of the problems can be found in Ref. [11]. An alternative method, developed at about the same time as the many-body approach, is the multiconfiguration Dirac-Fock (MCDF) formalism [12,13], a relativistic counterpart of the multiconfiguration Hartree-Fock (MCHF) method [14]. It is essentially a variational method similar to the "old-fashioned" configuration-interaction" (CI) formalism used in theoretical chemistry. This is at the basis of the present paper. We will now point out why in our view MCDF is an attractive alternative for the well-established many-body perturbation method (MBPT) and discuss the changes we have made in the MCDF procedure in order to include important advantages of the MBPT approach.

The perturbation method has the great advantage that one can take a certain (small) property, like hfi, as a perturbation and, using the many-body diagrammatic analysis, calculate just the modifications in the total wave function which contribute to the value of that property. Parts of the wave function, which are not contributing, are not calculated. The CI (MCDF) method optimizes the total energy functional and, with the component wave functions obtained, one can calculate many properties but this means that for getting a value for the hyperfine interaction of a certain atom one has to calculate many components of the wave function, important for the total energy, but maybe not for hfi. So it seems that using MCDF produces much overhead, by which we mean excessive analytical and computational effort not directly related to the property of interest. We will argue later that this is in general much less severe than it seems to be. There are other disadvantages which are more serious but these will be discussed later. The great power of MCDF, however, is the applicability to general open-shell systems for which the MBPT approach mentioned earlier is inadequate. The coupled-cluster theory [15] is a new development in this field, but the techniques are not yet well developed. This is in great contrast to MCDF, the techniques of which, thanks to the long CI history and the pioneering work of Grant [12], Desclaux, Mayers, and O'Brien [13], and especially Froese Fisher [14], are almost perfect. There are good computer codes available [16,17], so that nonspecialists can also do very advanced atomic calculations, an aspect which in our view is very important. We come now to the overhead of MCDF mentioned earlier. It was shown clearly by Kelly [1], and the detailed research of the group of Lindgren [9] that higher orders and in many cases even all orders in the perturbation expansion are required to explain certain experiments. This means that parts of the total wave function not contributing to hfi in lowest order become important in higher order by indirect effects (shifts in energy denominators are important examples). With this in mind the MCDF overhead is much less important. What remains to be done is to make the choice of components systematic (configurations) in the CI (MCDF) formalism. Based on our experience in MBPT we have formulated a code for analyzing the different contributions from MBPT in terms of configurations in MCDF. Other workers in the field use the MCDF formalism in a more indirect way: MBPT is formulated with MCDF based potentials, a quite different approach. For a recent paper see Ref. [18].

With our approach it is quite easy to perform lowest-order MBPT with MCDF techniques. We will call this MB-MCDF. Concerning higher-order MBPT it is our feeling that the coupled-cluster theory in practice can best be formulated in the MCDF framework.

We handle here particularly the lowest-order parts of MBPT, because of the transparency of these contributions and also because most of the calculations of hfi on heavy systems like Ra^+, using MBPT, are based on this part of the contributions and so it is possible to compare with results of other calculations. We have done two complete calculations with this method. The first application we considered is hyperfine interaction in Ra^+. This ion was taken because new experimental results are available on the hyperfine structure of Ra isotopes [19] and several MBPT calculations on the system [20,21] have been published, including a very recent one [22]. The second example is the hyperfine interaction of the $6p_{3/2}$ state of the thallium atom where until now MBPT could not give even an approximately correct explanation of the measured hfi constant [23,24]. The latter calculation is planned to be submitted as a separate paper. This paper is organized as follows.

First we discuss briefly the two methods MBPT and MCDF. In the second section the two methods are compared for single and double excitations. The third section gives a short outline of our method and the results for hfi in Ra^+. Comparison with other work and the discussion are given in the last section.

I. METHODS

The many-particle Hamiltonian is taken to be

$$H\Psi(r_1,\ldots,r_n)=E\Psi(r_1,\ldots,r_n)\ , \tag{1}$$

with

$$H=\sum_{i=1}^{n}\left[c\alpha_i\cdot\mathbf{p}_i+\beta_i mc^2-\frac{Ze^2}{r_i}\right]+\sum_{\substack{i,j\\ i>j=1}}^{n}\frac{e^2}{r_{ij}}\ . \tag{2}$$

c is the light velocity and α and β are the well-known 4×4 Dirac matrices. Equation (1) and the Hamiltonian (2) do not describe the physics of the atom completely, but it suffices for many purposes even though the potential energy term e^2/r_{ij} is even not approximately Lorentz invariant [12]. But it is the leading term in an expansion in powers of the fine-structure constant. The next term in this expansion, called the Breit interaction, is part of the radiative corrections necessary for a more correct description of the interactions between the electrons in the atom. See also Ref. [11] for a recent overview. However, here we can safely neglect these effects because for the hfi of the valence states of Ra^+, the influence is small. So we will follow the common practice by solving just Eq. (1), which in practice is finding a good approximation to this solution.

A. MCDF method

In order to solve Eq. (1) the total wave function Ψ is written as an, in principle, infinite series of terms Φ_j, which are determinants composed of n single-particle states φ_i:

$$\Psi(r_1,\ldots,r_n;J,M)=\sum_{j=1}^{N}C_j\Phi_j(\varphi_1,\varphi_2,\ldots,\varphi_n;J,M)\ , \tag{3}$$

where n is the number of electrons. The φ_i are coupled to lead to a final state with total angular momentum characterized by the quantum numbers J and M. Further, the following functional (variables are C_j and φ_i) is optimized:

$$E(\Psi)=\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}\ . \tag{4}$$

All orbitals φ_i in a certain configuration function Φ are orthonormal (not necessarily between separate Φ_j). In order to optimize $E(\Psi)$, one needs general expressions for the matrix elements of H between the functions Φ_j. These were derived by Grant in the 1960s [25] and subsequently several computer codes were developed. The most widely used is that of Desclaux [16].

The expansion (3) is the CI series of Ψ involving a finite number N of configurations with definite couplings of the separate one-electron quantum numbers j,m to the final J,M of the total wave function. This coupling can be extremely complex and it was Grant and co-workers who published a ready to use computer code to accomplish this task [26]. With this, the major techniques were also available for nonspecialists to do high level atomic calculations. Pair correlation was mostly not included in MCDF work, in contrast to the many publications based on MBPT. This is due to serious deficiencies in the existing MCDF codes. We found that it was possible to modify these codes using the work of Froese Fisher in nonrelativistic MCHF [17]. Further, we have added some minor options to the code so that certain important one-electron properties of current interest can be added to the Hamiltonian of Eq. (2). These are the following: (a) General polarization operator of the form

$$h=r^kC_q^k(\theta,\varphi)\ , \tag{5}$$

(b) The parity-violation operator [27]

$$h=G_F/(2\sqrt{2})Q_w\rho_N(r)\gamma_5\ , \tag{6}$$

and (c) the electric-dipole-moment operator [28]

$$h=2id_e\beta\gamma_5 c\bar{p}^{\,2}\ . \tag{7}$$

B. MBPT method

The MBPT method is more difficult to explain briefly but we will give here some of the major aspects. One has to consult Refs. [1–8] for more in-depth information.

Again the problem is to solve Eq. (1). We split the operator H into two parts, a good approximate one H_0 of which we know the solutions precisely:

$$H_0\Phi_\mu=E_\mu\Phi_\mu\ , \tag{8}$$

and a part (the perturbation) ΔH, which is the difference of the true Hamiltonian H and the approximate one H_0. We take H_0 to have the form

$$H_0=\sum_{i=1}^{n}\left[c\alpha_i\cdot\mathbf{p}_i+\beta_i mc^2-\frac{Ze^2}{r_i}+V(r_i)\right] \tag{9}$$

and

$$\Delta H=\sum_{\substack{i,j\\ i>j=1}}^{n}\frac{e^2}{r_{ij}}-\sum_{i=1}^{n}V(r_i)\ . \tag{10}$$

So we see that H_0 is chosen to be of the independent-particle type, involving the single-particle potential V. For simplicity we take the Φ_μ here to be single determinantal states composed of products of n single-particle φ_i, as we did in MCDF. However, the Φ_μ are not coupled. The φ_i are generated form

$$h_0\varphi_i=\varepsilon_i\varphi_i \tag{11a}$$

with

$$h_0=c\alpha\cdot\mathbf{p}+\beta mc^2+V(r)-\frac{Ze^2}{r}\ . \tag{11b}$$

In order to get to MBPT we assume the state we are interested in is nondegenerate (closed shell or semiclosed shell), and after switching to the formalism of second-order quantization we can write down immediately the formal solution for Eq. (1):

$$|\Psi\rangle=\sum_{n(L)}\left[\frac{1}{E_0-H_0}\Delta H\right]^n|\Phi_0\rangle\ . \tag{12a}$$

H_0 is the "vacuum" state satisfying

$$H_0|\Phi_0\rangle=E_0|\Phi_0\rangle\ , \tag{12b}$$

and actually it is the lowest-order approximation to the required solution. Equation (12a) is the so-called linked-cluster expansion of the final solution of Eq. (1) [29]. The L in Eq. (12a) means linked cluster. The interpretation of (12a) needs some comments, however. Because of the formalism of second-order quantization, the wave functions Ψ and Φ are now operator expressions instead of scalars and also the variables H_0 and ΔH are operators. Only E_0 is a scalar constant. The state vector $|\Psi\rangle$ is normalized as follows:

$$\langle\Phi_0|\Psi\rangle=1\ , \tag{13}$$

and the total energy $E=E_0+\Delta E$ is obtained formally [29] from

$$\Delta E=\langle\Phi_0|\Delta H|\Psi\rangle\ . \tag{14}$$

If we are interested in some property X, which commutes with H, we have

$$|X|=\langle\Phi_0|X|\Psi\rangle\ . \tag{15}$$

If X does not commute with H we have

$$|X|=\sum_{n,m}\langle\Psi^{(n)}|X|\Psi^{(m)}\rangle \tag{16}$$

with

$$\langle\Psi^{(n)}|=\left[\frac{\Delta H}{E_0-H_0}\right]_L^n|\Phi_0\rangle\ . \tag{17}$$

This formalism looks very powerful and simple. In practice, however, it is very tedious and no good computer codes are available to make this work for nonspecialists.

Concluding this section we would like to simplify the formulas above and make some preparation for the discussion of the link with MCDF. For this we take $n=1$ and find from (12)

$$(E_0-H_0)|\Psi^{(1)}\rangle=(\Delta H)_L|\Phi_0\rangle\ . \tag{18}$$

As shown by Lindgren and Morrison [9], this can be generalized to all orders. The special advantage of Eq. (18) is that it leads to a series of coupled differential equations for which good codes are available, whereas the form (12) requires the generation of large basis sets for the evaluation of the $1/(E_0-H_0)$ terms. Now we can write Eq. (18) in coordinate space by working out the operators and we find

$$\begin{aligned}(E_0-H_0)\Psi^{(1)}(r_1,\ldots,r_n)&=\Delta H\Phi_0(r_1,\ldots,r_n)\\&\quad-\langle\Phi_0|\Delta H|\Phi_0\rangle\\&\quad\times\Phi_0(r_1,\ldots,r_n)\ .\end{aligned} \tag{19}$$

H_0 is the scalar expression of Eq. (9). If now we take ΔH different from Eq. (10), simply to be a correction to the one-electron potential (for instance, the nuclear quadrupole interaction) we find Eq. (19) to lead to Sternheimer's one-particle equation [30]. So Eq. (18) is a generalized Sternheimer equation and it is one of the basic concepts of the successful MBPT approaches developed by the Chalmers group in the 1970s.

II. RELATION OF MCDF AND MBPT

Despite the fact that it is clear that the two approaches, taken to a sufficient degree of refinement, should give the same results, no papers have been found in which this actually was shown to happen. We assume this is because it is not at all clear to what level the calculations have to be taken in order to show the agreement.

For the comparison we consider MCDF (MCHF) as a special form of CI for which it is simpler to find the connection with MBPT. It is clear that if the fixed basis set of CI is equal to the (immense) basis set generated from the φ_i of Eqs. (11), the correspondence is obvious: CI is just another way of formulating MBPT, now formulated as an eigenvalue problem [31].

The energy optimalization in CI is only with respect to the CI coefficients; the basic functions are fixed. If now we also make the wave functions variables in the variational process, as is done in MCDF, it is clear the correspondence with MBPT becomes very complicated because we obtain linear combinations of the MBPT basic functions in all steps of the variational process. However, the ultimate results should be equal to those of CI because we only change the basis which anyhow should be complete. For many properties the series in Eq. (12a) is in practice very limited and first ($n=1$) and second ($n=2$) order in ΔH are enough for good results (a class of important higher-order corrections is included by shifted energy denominators, a common practice). This is the part of MBPT we will show to be clearly related to MCDF.

A. Single-particle excitations

We first establish a connection between MBPT, CI, and MCDF for terms of first order in ΔH of Eq. (10). This part is rather standard but it is given for completeness and it also serves as an introduction to the more complex second-order part.

1. MBPT equations

The Hamiltonian is taken to be

$$H=H_0+\Delta H_1+\Delta H_2\ , \tag{20}$$

with

$$\Delta H_1=\sum_{\substack{i,j\\ i>j}} 1/r_{ij}-\sum_i V(r_i) \tag{21}$$

and

$$\Delta H_2=\sum_i h_A(i)\ . \tag{22}$$

h_A is the hyperfine Hamiltonian:

$$h_A=\alpha\cdot(\boldsymbol{\mu}_I\times\mathbf{r})/r^3\ . \tag{23}$$

Equation (22) is only valid outside the nucleus. Inside the nucleus h_A is set equal to zero. We now take Eq. (12a) to second order in ΔH where ΔH is equal to the sum of ΔH_1 and ΔH_2 and derive an expression for ΔE which is second order in ΔH_1 and first order in the hyperfine term ΔH_2. It is straightforward to get, from Eqs. (12a) and (14),

$$\Delta E=\Delta E^{(1)}+\Delta E^{(2)}+\Delta E^{(3)}\ , \tag{24}$$

$$\Delta E^{(1)}=\langle\Phi_0|\Delta H_2|\Phi_0\rangle\ , \tag{25}$$

$$\begin{aligned}\Delta E^{(2)}&=\langle\Phi_0|\Delta H|\Psi^{(1)}\rangle\\ &=\left\langle\Phi_0\left|\Delta H_1\frac{\Delta H_2}{E_0-H_0}\right|\Phi_0\right\rangle\\ &\quad+\left\langle\Phi_0\left|\Delta H_2\frac{\Delta H_1}{E_0-H_0}\right|\Phi_0\right\rangle\ ,\end{aligned} \tag{26}$$

$$\begin{aligned}\Delta E^{(3)}&=\langle\Phi_0|\Delta H|\Psi^{(2)}\rangle\\ &=2\left\langle\Phi_0\left|\Delta H_2\frac{\Delta H_1}{E_0-H_0}\frac{\Delta H_1}{E_0-H_0}\right|\Phi_0\right\rangle\\ &\quad+\left\langle\Phi_0\left|\Delta H_1\frac{\Delta H_2}{E_0-H_0}\frac{\Delta H_1}{E_0-H_0}\right|\Phi_0\right\rangle\ .\end{aligned} \tag{27}$$

In all the operator fractions above, one has first to work out the numerator. We will now restrict ourselves to $\Delta E^{(2)}$ and so we have only single-particle excitations. In the next section we will handle the $\Delta E^{(3)}$ term.

In order to be less formal we take the case of Ra^+, where we have a valence orbital φ_a ($7s$, $7p_{1/2}$, or $7p_{3/2}$) outside closed shells ($6s,6p$). We can find from Eqs. (25) and (26) an expression for the hfi contribution.

$$\begin{aligned}\Delta E(\mathrm{hfi})&=\langle a|h_A|a\rangle\\ &\quad+2\sum_{b,i}\left[\frac{\langle a,b|1/r_{12}|a,i\rangle}{\varepsilon_b-\varepsilon_i}-\frac{\langle a,b|1/r_{12}|i,a\rangle}{\varepsilon_b-\varepsilon_i}\right.\\ &\quad\left.-\frac{\langle b|v_a|i\rangle}{\varepsilon_b-\varepsilon_i}\right]\langle i|h_A|b\rangle\ ,\end{aligned} \tag{28}$$

where v_a is the part of the potential V of Eq. (21) coming from orbital a. The symbol b represents the closed-shell orbitals and i an excited-state orbital chosen from the MBPT basis set. The orbitals are those introduced in Eq. (11).

It is common practice to use Feynman graphs to represent these terms. In Fig. 1 we give these diagrams in the form introduced by the group of Das [2,4].

2. CI equations

We set up the CI formalism in such a way that the relation with MBPT can easily be established. The expression to optimize is that given in Eq. (4). As introduced in Sec. I A we use

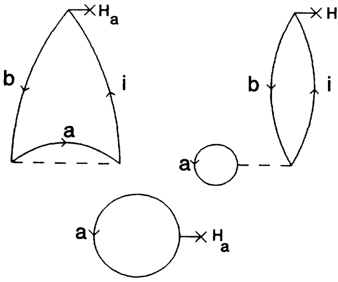

FIG. 1. Diagrammatic representation of contributions to hfi in Ra^+, up to first order.

$$H=H_0+\Delta H_1+\Delta H_2 \ , \tag{29}$$

with H_0, ΔH_1, and ΔH_2 as defined in Eqs. (9), (21), and (22), respectively. The final solution of the system is written as

$$\Psi=\sum_{\mu} C_\mu \Phi_\mu \ . \tag{30}$$

The subscript μ indexes all replacements $b \Longrightarrow i$ introduced in Eq. (28). So Φ_1 is the ground-state determinantal wave function or any other state of interest formulated as a simple determinantal wave function and the other Φ_μ are formed by replacing one of the orbitals φ_b (1*s* to 6*p* in Ra^+ case) by orbital φ_i out of a fixed set. In contrast to regular CI the Φ_μ ($\mu>1$) are not formulated as eigenfunctions of J^2 and J_z. This is because only in this way is the relation with MBPT transparent. The optimization is with respect to the coefficients C_μ. This gives the equations

$$\sum_{\nu} C_\nu H_{\mu\nu}=EC_\mu \ , \tag{31}$$

with

$$H_{\mu\nu}=\langle \Phi_\mu | H | \Phi_\nu \rangle \tag{32}$$

and

$$\sum_{\nu} C_\nu^* C_\nu=1 \ . \tag{33}$$

This is an eigenvalue problem. To make the connection with Eqs. (26) and (28) we have to expand C_μ and E in powers of $\Delta H(=\Delta H_1+\Delta H_2)$ and we get in second order

$$\Delta E^{(2)}=\sum_{\mu\,(>1)} \frac{\Delta H_{1\mu}\Delta H_{\mu 1}}{E_1-E_\mu} \ , \tag{34}$$

where as usual $E_\mu=\langle \Phi_\mu | H_0 | \Phi_\mu \rangle$. We can now safely replace E_1-E_μ by $\varepsilon_b-\varepsilon_i$, the ε being introduced in Eq. (11). After working out ΔH, we arrive at Eq. (28) for the contribution to hfi. It is worth noting that the discussion above only applies for systems for which a single determinantal Φ_1 can be defined as in our Ra^+ system. For our purpose this is no real restriction because most of the MBPT work is done for these systems. This serves as introduction to the comparison with MCDF, which is more complex.

3. *MCDF equations*

Again we optimize Eq. (4) but now also with respect to the wave functions Φ_μ introduced in Eq. (30). The variation in Φ_μ is realized by a variation in the orbital φ_i in the excitation $b \Longrightarrow i$ with φ_b fixed. We here restrict ourselves to first order (in ΔH_1) contributions to E; so no double excitations are considered here. We will come to these contributions in the next section. These optimized orbitals we will denote by $\hat{\varphi}_i$ to make a distinction with the earlier introduced φ_i. So every orbital φ_b creates its one and only $\hat{\varphi}_i$, which will be shown to be a simple linear combination of the φ_i in such a way that after substituting this linear combination, again Eq. (28) is found. The variation of $\hat{\varphi}_i$ is in the space orthogonal to all φ_b but not to other $\hat{\varphi}_j$.

The optimization with respect to Φ_μ leads to

$$\sum_{\mu} C_\mu (H-E)\Phi_\mu=0 \ . \tag{35}$$

This can be seen as a way of rewriting our problem as in Eq. (1) using a special expansion code. We will assume here that the Φ_μ are orthogonal, which is a valid one because of the way our Φ_μ are constructed (the $\hat{\varphi}_i$ need not be orthogonal).

It is important to realize that the basis set in Eq. (35) is very much smaller than the basis used in MBPT or CI. This is a result of the additional variation with respect to $\hat{\varphi}_i$. At this step we may assume the coefficients C_μ are known [see for this Eq. (31) of the CI description]. After expansion of E in powers of ΔH_1 and ΔH_2 and using the fact that in this step C_1 is unity and C_μ ($\mu>1$) is first order in ΔH_1 or ΔH_2 (denoted by subscripts μ and ν, respectively), we find the following equations which the Φ_μ have to satisfy:

$$\sum_{\mu\,(>1)} C_\mu (H_0-E_0)\Phi_\mu+(\Delta H_1-E_1)\Phi_1=0 \ , \tag{36}$$

$$\sum_{\nu\,(\neq\mu>1)} C_\nu (H_0-E_0)\Phi_\nu+(\Delta H_2-E_1)\Phi_1=0 \ . \tag{37}$$

The E_0, E_1, and E_2 are expectation values of H_0, ΔH_1, and ΔH_2 over the state function Φ_1.

The hfi term $\Delta E^{(2)}$ [see, Eq. (26)] is found from

$$\Delta E^{(2)}=\sum_{\mu} C_\mu \langle \Phi_1 | \Delta H_2 | \Phi_\mu \rangle+\sum_{\nu} C_\nu \langle \Phi_1 | \Delta H_1 | \Phi_\nu \rangle \ . \tag{38}$$

We now reduce to single-particle equations by rewriting H_0 as a sum of single-particle term h_0 and using Eqs. (21) and (22) for ΔH_1 and ΔH_2 (uncoupled Φ_μ are used):

$$\Phi_1=|\varphi_1,\varphi_2,\ldots,\varphi_n| \ , \tag{39a}$$

$$\Phi_{\mu\,(b\Longrightarrow i)}=|\varphi_1,\varphi_2,\ldots,\hat{\varphi}_i,\ldots,\varphi_n| \ , \tag{39b}$$

and

$$H=\sum_{i=1}^{n} h_0(i)+\Delta H_1+\Delta H_2 \ . \tag{40}$$

The only difficult term is the ΔH_1 term, but because we consider here only single-particle excitations, it is possible to write $\Delta H_1=\sum_i \Delta h_1(i)$ and so we find the following equations for the MCDF orbitals:

$$C_\mu (h_0-\varepsilon_b)\hat{\varphi}_{i(1)}+(\Delta h_1-e_1)\varphi_b=0 \ , \tag{41}$$

$$C_\nu (h_0-\varepsilon_b)\hat{\varphi}_{i(2)}+(h_A-e_2)\varphi_b=0 \ . \tag{42}$$

$\hat{\varphi}_{i(1)}$ is generated by ΔH_1 and $\hat{\varphi}_{i(2)}$ by ΔH_2. The constants e_1 and e_2 are similar to E_1 and E_2 introduced in Eqs. (36) and (37), ε_b is the orbital energy of φ_b ($h_0\varphi_b=\varepsilon_b\varphi_b$), and Δh_1 is defined by the following expression:

$$\Delta h_1 \varphi_b=\sum_{c} (\langle c | 1/r_{12} | c \rangle \varphi_b-\langle c | 1/r_{12} | b \rangle \varphi_c)-v_b\varphi_b \ . \tag{43}$$

In Eq. (43) v_b is the part of the potential V which comes from the interaction with orbital φ_c. This orbital can be any orbital (closed and opened); if V is chosen to be the Hartree-Fock potential, only $c=a$ remains. It is important to point out the fact that Eqs. (41) and (42) are similar to the so-called Sternheimer equation, which is part of the first level in the MBPT approach of the Chalmers group [11]. They were also referred to as moment-perturbed and exchange-perturbed equations by Das and co-workers [32]. The entity $C_\mu \hat{\varphi}_i$ plays the role of the $\rho(b \Longrightarrow i;r)$ function [8]. In order to satisfy the requirement of orthogonality to the other occupied state we have to add Lagrangian multipliers and these give additional terms in Eqs. (41) and (42). For the general discussion these are not very important, however.

4. *MCDF in practice*

It will be clear MCDF does not work as described above. It works with the complete Hamiltonian H and not with an H_0 and a ΔH. We have shown, however, that if the formalism is set up into perturbational steps, the relation with other approaches can be made quite simply. After closer inspection of the MCHF equations one can show the following facts.

(a) The potential used in Eqs. (41) and (42) is of V^{n-1} form, in contrast with what may be concluded from the equations given above, where φ_b is an eigenfunction of h_0.

(b) The parameter ε_b in the MCDF equations is a free parameter ε. However, from the preceding formalism one can find a relation between this free parameter and ε_b, at least if the perturbation ΔH is small. Actually it comes out that ε_b is a good approximation for this "free" parameter, because φ_b comes out to be a good approximation for an eigenfunction of h_0.

These findings are very important in MCDF practice because it is well known a V^{n-1} potential form is crucial for fast convergence in the wave-function expansion (better virtuals) and secondly a fixed energy parameter or a good approximation to it was found to be crucial for damping instabilities in finding the solutions of Eqs. (41) and (42). This ends our formal discussion of single-particle effects.

B. Two-particle excitations

We arrive now at the most important part of our discussion: consideration of effects one order higher in ΔH_1, which introduces correlation effects and other effects which are the result of two-particle excitations as formally introduced in Eq. (27). We will find a two-particle equation similar to the pair equation used in the earlier work of Mårtensson [33], but now solved within the MCDF formalism. The correspondence and differences between this approach and the basis-set MBPT approach will be discussed.

1. *MBPT equations*

First we start with MBPT in the basis-set form. Although in second order there are also single excitations contributing, we will focus on the pair excitations. So we define the excitations $c,b \Longrightarrow i_1,i_2,\ldots$, where c can be the open-shell orbital or a closed-shell orbital and b is only a closed-shell orbital. The i orbitals include the virtual space of the open shell.

From Eq. (27) we find

$$\Delta E_1^{(3)} = -\sum_{c,b,i} \frac{\langle c_2,b|\,|i_1,i_2\rangle\langle c_1|h_A|c_2\rangle\langle i_1,i_2|\,|c_1,b\rangle}{(\varepsilon_{c_1}+\varepsilon_b-\varepsilon_{i_1}-\varepsilon_{i_2})(\varepsilon_{c_2}+\varepsilon_b-\varepsilon_{i_1}-\varepsilon_{i_2})} + \sum_{c,b,i} \frac{\langle c,b|\,|i_3,i_2\rangle\langle i_3|h_A|i_1\rangle\langle i_1,i_2|\,|c,b\rangle}{(\varepsilon_c+\varepsilon_b-\varepsilon_{i_1}-\varepsilon_{i_2})(\varepsilon_c+\varepsilon_b-\varepsilon_{i_3}-\varepsilon_{i_2})} + \cdots , \tag{44}$$

$$\Delta E_2^{(3)} = 2\sum_{c,b,i} \frac{\langle c|h_A|i_3\rangle\langle i_3,b|\,|i_1,i_2\rangle\langle i_1,i_2|\,|c,b\rangle}{(\varepsilon_c-\varepsilon_{i_3})(\varepsilon_c+\varepsilon_b-\varepsilon_{i_1}-\varepsilon_{i_2})} - 2\sum_{c,b,i} \frac{\langle c_2|h_A|i_1\rangle\langle c_1,b|\,|c_2,i_2\rangle\langle i_1,i_2|\,|c_1,b\rangle}{(\varepsilon_{c_2}-\varepsilon_{i_1})(\varepsilon_b+\varepsilon_{c_1}-\varepsilon_{i_1}-\varepsilon_{i_2}} + \ldots , \tag{45}$$

where the ellipsis represents exchange. In the equations above c can be interchanged with b and the summations are over all orbital indices. We have classified the correlation contributions in our case (Ra$^+$) in two classes: one, ΔE_1, where the hfi is sandwiched between two $1/r_{12}$ interaction elements, denoted by the $|\,|$ symbol and one, ΔE_2, where we have two subsequent $1/r_{12}$ interaction elements resulting in a single excitation and the hfi being the last element (from right to left). It is common practice to give Feynman diagrams instead of the equations above but because this paper is primarily MCDF-like and in this field these techniques are usually not used, we have given the equations. The corresponding diagrams are drawn in Fig. 2. The Das convention for diagrams is used. With this convention ΔE_1 corresponds to the (11)-

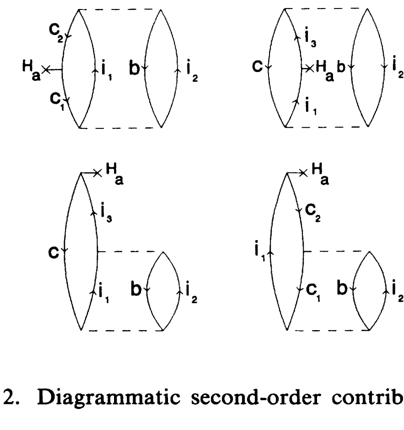

FIG. 2. Diagrammatic second-order contributions to hfi in Ra$^+$.

type diagrams and ΔE_2 to the (02) diagrams. We now turn to the comparison with CI and MCDF.

2. CI equations

It is straightforward to extend the formalism for CI given in Sec. II B to third order. We find the following expression for $\Delta E^{(3)}$:

$$\Delta E^{(3)}=\sum_{\substack{\mu,\mu' \\ (>1)}} \frac{\Delta H_{1\mu'}(\Delta H_{\mu'\mu}-E^{(1)}\delta_{\mu'\mu})\Delta H_{\mu 1}}{(E_1-E_\mu)(E_1-E_{\mu'})} , \qquad (46)$$

with

$$\Delta H=\Delta H_1+\Delta H_2 \qquad (47)$$

and

$$E^{(1)}=\Delta H_{11} . \qquad (48)$$

The Φ_μ are found from Φ_1 ($=\Phi_0$) by making double excitations: $\Phi_{\mu\neq 1}=\Phi_1(b_1\Longrightarrow i_1, b_2\Longrightarrow i_2)$, with all other orbitals fixed. After reducing to single-particle equations one finds again Eq. (44). Equation (45) is found from two subsequent pair excitations resulting in a single excitation of the form introduced in Sec. II. So in order to obtain this from Eq. (46), we have to include also single excitation in the set Φ_μ.

3. MCDF equations

In MCDF things are rather different, because we have to define the functional derivative with respect to a two-particle wave function. The starting equation is again

$$H\sum_\mu C_\mu \phi_\mu=E\sum_\mu C_\mu \Phi_\mu \qquad (49)$$

with C_μ fixed (found from earlier cycle) and the Φ_μ are obtained from pair excitations $b_1,b_2\Longrightarrow r,s$ where r and s denote the angular character of the two coordinate spaces $\bar{r}_1$ and $\bar{r}_2$. The radial character of the r,s function is not necessarily formulated as a product of two separate coordinate spaces.

If we sort out a certain pair $b_1,b_2\Longrightarrow r,s$ we can multiply Eq. (49) with all other orbitals and integrate the left- and right-hand sides over all the corresponding coordinates and we are left with a differential equation for that pair:

$$[\varepsilon_1+\varepsilon_2-h_0(1)-h_0(2)]C_{\mu(rs)}U_{rs} = (1/r_{12})C_1\varphi_{b_1}\varphi_{b_2}-\Delta\varepsilon_{12}C_1\varphi_{b_1}\varphi_{b_2} , \qquad (50)$$

where

$$\Delta\varepsilon_{12}=\langle\varphi_{b_1}\varphi_{b_2}|1/r_{12}|\varphi_{b_1}\varphi_{b_2}\rangle-\langle\varphi_{b_1}\varphi_{b_2}|1/r_{12}|\varphi_{b_2}\varphi_{b_1}\rangle , \qquad (51)$$

and ε_1 and ε_2 are the orbital energies of φ_{b_1} and φ_{b_2}.

In order to obtain (50) we have introduced the pair function U_{rs}, belonging to a certain J value. It can be formulated as a coupled product of two excited φ_i's. Further we use the perturbation philosophy introduced earlier; so ε_1 and ε_2 are the orbital energies of the parent orbitals φ_{b_1} and φ_{b_2} as eigenfunctions of h_0 with potential V [see Eq. (40)]. These orbitals are coupled to the same J value as that of U_{rs}. Equation (50) is similar to the equation of Mårtensson [33], the main modification being the occurrence of coupled $C_\mu U_{rs}$ instead of the usual radial pair function (U_{rs} is normalized). If now we expand this function as follows:

$$C_\mu U_{rs}=\sum_{i,j} a_{ij}\varphi_i(r_1)\varphi_j(r_2) , \qquad (52)$$

the relation with the MBPT basis-set formalism can be found by identifying the φ_i with the fixed (large) basis set, the coupling being the main difference.

As shown extensively by Mårtensson, solving (50) directly is a much more efficient way to calculate the results of this pair function. However, the two-dimensional integration and the inherent problems in relativistic formalism make this method not very practical. In MCDF Eq. (50) is solved by taking U_{rs} to be the product of two functions φ_r and φ_s and this avoids most of the problems with relativistic formulation [11].

4. MCDF in practice

The equation which is actually being solved in MCDF is somewhat different from (50). First the basis functions φ_b are not eigenfunctions of an h_0 in the sense of MBPT but if the C_μ are small they are well approximated by considering them as eigenfunctions of a certain HF-like h_0. Secondly in the MCDF equations the sum $\varepsilon_1+\varepsilon_2$ looks like

$$\varepsilon_1+\varepsilon_2-\langle\varphi_{b_1}\varphi_{b_2}|1/r_{12}|\varphi_{b_1}\varphi_{b_2}\rangle+\cdots$$

where the ellipsis represents exchange. The $1/r_{12}$ term is the first of several "higher-order" effects directly included in the MCDF formalism. In MBPT it has to be added in a separate step. Another difference is the interaction between the excited φ_r and φ_s, which is included and does not require a separate step. Now we make some final notes on the practice of solving Eq. (50). In this equation we substitute

$$U_{rs}=\varphi_r(\mathbf{r}_1)\varphi_s(\mathbf{r}_2) \qquad (53)$$

where the quantum numbers j_1 and j_2 of φ_r and φ_s are coupled to a certain j_{12}. After working out the angular dependence, we first multiply with the radial part of φ_s and integrate in order to get an equation for the radial part of φ_r. The process is repeated for φ_s. It will be clear that the constants ε_1 and ε_2 become free parameters which are now not close to orbital energies of the parent orbitals, as in the case of single excitations. The contribution to the hfi can formally be obtained from

$$\Delta E^{(3)}=\sum_{\mu(\neq 1)} C_\mu\langle\Phi_\mu|\Delta H_2|\Phi_\mu\rangle +2\sum_{\mu'\neq 1} C_{\mu'}\langle\Phi_1|\Delta H_2|\Phi_{\mu'}\rangle . \qquad (54)$$

The "constants" C_μ can be approximated by

$$C_\mu = \frac{\langle \Phi_1 | \Delta H_1 | \Phi_\mu \rangle}{\langle \Phi_1 | H_0 | \Phi_1 \rangle - \langle \Phi_\mu | H_0 | \Phi_\mu \rangle} , \tag{55}$$

a first-order approximation.

The set μ' is the result of two subsequent pair excitations mentioned earlier and $C_{\mu'}$ can be expressed as a second-order (in ΔH_1) approximation similar to Eq. (55). It is important to mention here that our wave function Φ_1 is modified only by ΔH_1 and not by ΔH_2(hfi). We end this discussion by pointing to the fact that because of coupling our final equations are different from the MBPT equations (44) and (45). As was mentioned by introducing the pair function U_{rs}, this function belongs to a definite value of the pair angular momentum j_{12}. Because j_{12} can in general have more than one value, there are a number of φ_r, φ_s pair orbitals. This has some relation with the formalism of Mårtensson [33], where the angular momenta of the functions φ_r and φ_s are also coupled using the angular momentum variable k arising from the expansion of $1/r_{12}$. Further, the excitation $b_1, b_2 \Longrightarrow r, s$ is handled independent of the excitation $b_1, b_2 \Longrightarrow s, r$. In MCDF, however, one usually uses the same wave functions for all values of j_{12}. This is the main reason why certain contributions to hfi in the MCDF formalism can be very different from those of MBPT. We will discuss this in Sec. VI.

III. RESULTS

The results of the hfi in Ra$^+$ were obtained with a modification of the standard MCDF procedure which we now briefly describe.

A. MB-MCDF approach

The following steps define the approach.

1. MBPT analysis (using Feynman diagrams) of the contributions to second order in the $1/r_{12}$ interaction.
2. Definition of the configurations required.
3. Calculation of the angular factors for the interaction elements using the code of Grant *et al.* [26]. An interface written by one of us (v.d.B.) was used to transform the results to the format of the code of Desclaux, Mayers, and O'Brien [13].
4. Calculation of the actual contributions using the Desclaux code (modified).

The most important obstacle in MCDF practice is the inherent instability in solving the nonlinear coupled equations. Froese Fisher [14] has published many papers on the subject and solved the problem almost completely, at least in nonrelativistic formalism. So we transformed her ideas to the MCDF equations and found this worked quite well in getting the most difficult part of the basic orbitals: the correlation orbitals (required for the pair function).

Another important modification we introduced was making the option of fixed energy parameters, which is crucial for getting the single excitations efficiently, but was found to be also very helpful for the correlation orbitals. Details of these modifications can be obtained on request.

B. hfi in Ra$^+$

The contributions to the hfi in Ra$^+$ are divided into three classes.

a. Hartree-Fock (HF). We generalize this contribution to that of the lowest-order contribution of the valence electron in some average field Hamiltonian h_0. In Refs. [20] and [21] the core orbitals were generated for a Ra^{2+} ion, whereas in this work the core orbitals are for Ra$^+$ in accordance with Ref. [22].

b. Polarization. This class includes all polarizations of the core resulting from the open-shell character of the valence electron. For simplicity it is denoted by ECP (exchange core polarization), but direct effects are included.

c. Correlation. This class includes all contributions, where double excitations play a role. As introduced earlier there are two types. 1. The first one is denoted by $|1/r_{12}|\text{hfi}|1/r_{12}|$: the sandwich type. $|1/r_{12}|$ is short for the pair excitation involved. 2 The second one is actually of the polarization type, but now of second order in $1/r_{12}$. It will be denoted by $|\text{hfi}|1/r_{12}|1/r_{12}|$. So one has to apply two pair excitations sequentially to obtain a single excitation. An important subclass is formed by the so-called Brueckner-orbital effects [9]. Actually Brueckner orbitals can be calculated in the MCDF formalism.

The basic excitations used in evaluating the contributions are given in Table I. In the table the $1s$-$6s \Longrightarrow ns$, for instance, means excitations of $1s$-$6s$ to different (not necessarily orthogonal) states ($8s$, $9s$, etc.). We see from Table I that the correlation is restricted to the $n = 6$ shell, that is, the shell of occupied states just below the valence electron shell. Experience has shown that this is good enough for a system like Ra$^+$. However, the polarizations have to be calculated for all shells and we also did lowest order consistency for s,p and p,s cross terms.

Further, we did not use all the excitations shown in Table I for all three states. For the $7s$ state, for instance, only a few contributions are sizeable whereas for the $7p_{3/2}$ state many contributions are important. The reason is obvious: $7s$ itself being an s state has a large contribution to hfi and polarizations of p shells are relatively much less important than polarizations of s shells for the $7p_{3/2}$ state, because $7p_{3/2}$ has a small hfi. The excitations used will be shown in the table of results. We have decided to give detailed information on separate contributions, because our experience is that giving final results without giving details of the procedure by which they were derived is of relatively less value for the reader,

TABLE I. Basic excitations of the MB-MCDF calculation of hfi in Ra$^+$.

Polarization	$1s$-$6s \Longrightarrow ns$
	$2p$-$6p \Longrightarrow np$
	$3d$-$5d \Longrightarrow nd$
Correlation	$6s,6p,7s,7p \Longrightarrow ns,np,nd,nf,ng$

TABLE II. Results of hfi constant in ^{221}Ra II for the 7*s* and $7p_{1/2}$ states. Values are in MHz.

		7*s*		$7p_{1/2}$
Type				
HF[a]		−1089.0		−182.6
ECP	*s*	−192.8		7.2
	p	19.5		−41.4
Consistency[b]		−5.6		−1.3
Correlation (1)			$1/r_{12}\|hfi\|1/r_{12}\|$	
$7s6p \Longrightarrow sp$		−8.7	$7p6p \Longrightarrow ss$	0.4
			sd	2.2
			dd	0.9
Correlation (2)			$\|hfi\|1/r_{12}\|1/r_{12}\|$	
$7s6p \Longrightarrow sp$		−44.9	$6p6s \Longrightarrow pd$	−0.8
pd		−78.1	$7p6s \Longrightarrow pd$	0.4
			$7p6p \Longrightarrow sd$	−18.2
			dd	−18.2
			dg	−0.9
			pp	−5.2
			pf	−2.6
Normalization[c]		15.6		2.8
Total		−1384.0		−258.6
Expt.[d]		−1348.6		−266.3

[a] The magnetic hfi inside the nucleus is neglected.

[b] The consistency contribution includes here indirect effects: one polarized orbital polarizes another one (*ss* and *sp*).

[c] The normalization contribution is a result of the decrease in the valence shell contribution because C_1 of Eq. (49) becomes smaller than one.

[d] Reference [19].

because then one cannot have an understanding of the origin of the error bar involved. Also for other workers in the field there is no way to make significant comparison with the result of the present work.

TABLE III. Results of magnetic (*A*) and electric (*B/Q*) hfi coupling of the $7p_{3/2}$ state of ^{221}Ra II. Values are in Mhz and MHz/barn, respectively.

		A		*B/Q*
Type				
HF		−13.9		413.8
ECP	*s*	−4.12	*sd*	3.0
	p	−3.11	*pp*	212.9
			dd	6.4
Consistency		−0.70		5.0
Correlation (1)			$\|1/r_{12}\|hfi\|1/r_{12}\|$	
$7s6p \Longrightarrow ss$		−0.33	small	
sd		−0.15		
dd		−0.20		
Correlation (2)			$\|hfi\|1/r_{12}\|1/r_{12}\|$	
$6p6s \Longrightarrow pd$		0.46	small	
$7p6s \Longrightarrow pd$		−0.11		
$7p6p \Longrightarrow ss$				
sd		0.45	$7p6p \Longrightarrow sd$	23.2
dd		−0.56	*dd*	17.9
pp		−0.24	*pp*	6.0
dg		−0.04		
pf		−0.10		
Normalization		0.10		−4.0
Total		−22.55		684.2
Expt.		−22.4		689.7

The effects given above can be calculated in two ways: (1) Fix all orbitals to those of the zero-order Hamiltonian (here this means MCDF without interactions) and (2) Let all orbitals be free to adjust after adding the interactions.

We mainly used the first approach because it gives more insight into the mechanisms involved. Additionally the second approach introduces higher-order effects which are beyond our present scope. The results are given in Tables II and III.

TABLE IV. Comparison of hfi result Ra II calculated by different authors. *A* is the magnetic and *B/Q* the electric hfi constant. Results are in MHz and Mhz/barn, respectively.

	Contributions Direct	ECP	Correlation	Sum
7*s* (*A*)	−1089.0	−179.0	−116.0	−1384.0
Ref. [20]	−1055.0	−172.0		
[21]	−1032.0	−171.0	−162.0	−1365.0
[22]	−1047.0	−144.5	−136.9	−1328.4
$7p_{1/2}$ (*A*)	−182.6	−33.9	−34.2	−257.3
Ref. [20]	−176.6	−34.1		
[21]	−173.2	−31.9	−56.7	−261.8
$7p_{3/2}$ (*A*)	−13.9	−7.93	−0.72	−22.55
Ref. [20]	−13.3	−8.85		
[21]	−13.3	−8.42	−0.56	−22.29
$7p_{3/2}$ (*B/Q*)	413.8	227.2	43.1	684.2
Ref. [20]	401	234		674

IV. DISCUSSION AND CONCLUSIONS

From our Tables II and III we see a satisfactory explanation of the measured hfi constants. It is obvious our MB-MCDF formalism works quite well for this type of calculations. The calculation of hfi in systems with one electron outside closed shells like our present Ra^{+} system has been almost exclusively the domain of the MBPT approach. MCDF has not been so successful yet. With this work we have shown MCDF can do the job equally well. However, the work involved has been found to be much less than that required for a basis-set MBPT. We have shown that a formal relation exists with other approaches and we will now also compare the result with those published earlier. In Table IV we give a direct comparison of distinct contributions of which unfortunately there are not so many.

We can see there is good agreement on the HF and ECP values, but substantial disagreement is found for the correlation part. The differences are partly due to the fact that the correlation contribution is small and because Refs. [20] and [21] use a Ra^{2+} potential for the core orbitals a small correction to this potential may show up as a relatively large modification of the correlation part. This is particularly clear for the $7s$ state, where the difference in the HF values equals more or less the correlation difference.

For the $7p_{3/2}$ state the difference is almost certainly due to the different handling of exchange contribution as mentioned earlier in this paper, but is clearly not serious for the final result. It is important to mention here that for this state there is strong cancellation of large contributions of opposite signs.

For the $7p_{1/2}$ state the two sources will both be active because the difference in the HF value is only partly covered by a change in the correlation contribution.

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