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RELCI: A program for relativistic configuration interaction calculations ☆

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Abstract

The set-up and diagonalization of (large) Hamiltonian matrices are two *key elements* in studying the structure and properties of many-electron atoms and ions. The efficiency in dealing with these tasks eventually determines for which atomic systems useful ab initio predictions can be made today and how accurate these predictions are. To facilitate further structure calculations, in particular for open-shell atoms and ions, here we present a new configuration interaction program in the framework of the RATIP package which help incorporate different approximations to the electron–electron interaction in the Hamiltonian matrix and, thus, into the representation of the wave functions. Our new program also supports several computational modes to allow for a flexible choice between particular time and storage requirements of the user. Care has been taken to provide a modern and user-friendly component of the RATIP package which carefully applies the concepts of Fortran 90/95.

PROGRAM SUMMARY

Title of program: RELCI

Catalogue identifier: ADQH

Program Summary URL: http://cpc.cs.qub.ac.uk/summaries/ADQH

Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland

Licensing provisions: None

Computer on which the program has been tested: IBM RS 6000, PC Pentium III; *Installations*: University of Kassel (Germany)

Operating systems: IBM AIX 4.1.2+, Linux 6.1.+

Program language used: ANSI standard Fortran 90/95

Memory required to execute with typical data: memory requirements strongly depend on the size of the Hamiltonian matrix and the selected mode of computation

No. of bits in a word: All real variables are parametrized by a `selected kind parameter` and, thus, can easily be adapted to

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☆ This program can be downloaded from the CPC Program Library under catalogue identifier: http://cpc.cs.qub.ac.uk/summaries/ADQH

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any required precision as supported by the compiler. Presently, the `kind` parameter is set to double precision (two 32-bit words) in the module `rabs_constant`

Peripheral used: disk for input/output

CPU time required to execute test data: 8 min on a 550 MHz Pentium III processor

No. of bytes in distributed program, including test data, etc.: 3 509 407

Distribution format: tar gzip file

CPC Program Library subprograms required: Catalogue number: ADCU; Title: GRASP92; Refs. in CPC: 94 (1996) 249

Keywords: Atomic, Breit interaction, configuration interaction, Dirac–Coulomb–Breit Hamiltonian, large-scale computations, multiconfiguration Dirac–Fock, QED estimate, relativistic, transverse interaction

Nature of the physical problem
Approximate atomic wave functions are determined by diagonalizing the Hamiltonian matrix within an appropriate many-particle basis. Here, the construction of the configuration interaction (CI) basis follows the same principles as in the structure code GRASP92 [1] which is utilized to generate the configuration state functions (CSF) and the radial orbitals for all subshells of the given active space.

Restrictions onto the complexity of the problem
The size of useful CI expansions critically depends on the shell structure of the atom or ion under consideration. Wave function expansions of several ten (or even hundred) thousand CSF are currently feasible on standard PCs. For more than two *equivalent* electrons, antisymmetrized subshell states are supported only for $j \leqslant 9/2$ (i.e. for all shells up to the $g_{9/2}$ or $h_{9/2}$ subshells).

Unusual features of the program
RELCI is designed as part of the RATIP package [2,3] for the calculation of relativistic atomic transition and ionization properties. An interactive dialog at the beginning of the execution enables the user to specify the (relativistic) interactions among the electrons and the mode of computation. A number of different modes are supported with regard to the *re-use* and maintenance of the internal storage. While the implementation of the program follows lines similar to GRASP92, still, the RELCI program has been rewritten entirely to conform to the new Fortran 90/95 standard [4] and to meet the requirements of modern applications. By using a dynamic allocation of all important arrays, there are no restrictions any more with regard to the numbers of open shells (within a single CSF) or individual subshells. When compared with RCI92 for their run-time behaviour, our new RELCI program is faster by a factor between $3 \ldots 8$, depending on the particular application.

References

[1] F.A. Parpia, C.F. Fischer, I.P. Grant, Comput. Phys. Commun. 94 (1996) 249.
[2] S. Fritzsche, J. Elec. Spec. Rel. Phen. 114–116 (2001) 1155.
[3] S. Fritzsche, C.F. Fischer, C.Z. Dong, Comput. Phys. Commun. 124 (2000) 343.
[4] M. Metcalf, J. Reid, Fortran 90/95 Explained, Oxford University Press, 1996.

LONG WRITE-UP

1. Large-scale configuration interaction calculations

Relativistic calculations on the electronic structure of atoms and ions have been carried out for more than 30 years. As well as providing a better understanding of the level structure and the properties of heavy and superheavy elements, today these computations serve primarily to provide accurate data which are difficult to obtain otherwise. In astro and plasma physics, for example, many models rely on the knowledge of atomic data for multiple- and highly-charged ions whose generation need to be based on a relativistic theory. Apart from these *traditional* fields, however, there are many other research areas with quite similar requirements on the accuracy of the data such as vuv- and X-ray lithography, quantum optics, material science or even the search for more efficient X-ray laser schemes.

Several methods are known today for studying the structure and properties of atoms and ions. In relativistic theory, two widely applied techniques are the (relativistic) configuration interaction (CI) and the multiconfiguration Dirac–Fock (MCDF) methods both of which have the advantage that they can easily be applied to excited and open-shell atoms across the whole periodic table. The (wide) range of applications of these two methods is in contrast to most variants of many-body perturbation theory which are often restricted to simple shell structures with only a very few electrons or holes outside of otherwise closed shells. Over the years, therefore, the implementation of the CI and MCDF methods has led to several powerful codes including, for example, Desclaux's program [1] or the well-known GRASP code [2,3].

Typically, the standard codes like GRASP92 [3] provide (approximate) energies and wave functions for a selected number of atomic bound states. Less attention in the development of these programs was paid originally to an efficient computation of atomic properties other than the total energies of free atoms and ions, utilizing these wave function expansions. The computation of such properties has been emphasized recently, though. In our group in Kassel, for instance, we developed the RATIP package [4,5] which applies the wave functions from GRASP92 and, meanwhile, provides a powerful tool for the study of various atomic properties. Apart from (the still increasing demand on) transition probabilities and lifetimes, this package recently helped us to investigate the scattering [6] and Auger emission [7] of electrons as well as the *coherence transfer* through the Auger cascades of resonantly-excited noble gases [8,9].

With the increasing number of case studies during the last few years, however, it became obvious, both in nonrelativistic and relativistic applications, that accurate predictions often require *large-scale* computations. For open-shell atoms and ions, in fact, very sizeable or even huge wave function expansions may arise and are, still, the main reason that (almost) no reliable ab initio computations exist for open d- and f-shell elements. Although some improvement of this situation can be expected in the future due to more powerful computers, of equal importance seems to us the development of proper tools since just a few programs are capable today of dealing with *systematic* investigations for such open-shell structures. In the case of the widely applied GRASP92 package, for example, several known shortcomings concern (i) the storage management and the portability of the code and (ii) the computation of the angular integrals whose (original) implementation dates back for more than 30 years.

Therefore, to facilitate the generation of large wave function expansion for complex shell structures, here we present RELCI, a new relativistic CI program. This program has been designed as a new component of the RATIP package [4,5] to allow for expansions of several ten thousand configuration state functions (CSF). In the future, this number is expected to increase as more powerful computers will become available. As appropriate for large-scale applications, moreover, we also support a number of different computational models in RELCI with regard to the internal storage and time requirements. When compared with RCI92 [3], the CI component of GRASP92, our new program clearly reduces the necessary resources. In typical applications, for instance, the CPU time is reduced by a factor between $3 \ldots 8$.

In the following section, we provide the reader with some theoretical background of the relativistic (atomic) CI method. This includes a short discussion of the electron–electron interaction which gives rise to the different choices of the Hamiltonian in relativistic computations. Since, however, most of this material can be found in the literature (although in different contexts) we shall focus on such aspects which differ from previous CI implementations. Emphasis has been paid especially to the decomposition of the Hamiltonian matrix into one- and two-particle amplitudes as well as to an alternative way, as suggested by Kim [10], for estimating the total self-energy contribution in many-electron computations. For a discussion of the *angular integration* in the set-up of the Hamiltonian matrix, however, we refer the reader to a recent article by Gaigalas et al. [11]. Section 3, then, describes the program structure of RELCI and how the code is distributed. Because RELCI will become a part of the RATIP program, we could make use of several previously-published *modules* as well as of Fortran 90/95's powerful features. The example in Section 4, later, describes a test calculation on the level structure of multiple-charged Fe^{9+} ions while a brief run-time comparison with RCI92 is made in Section 5. Finally, a short summary will be given in Section 6.

2. Theoretical background

In its standard form, the configuration interaction method implies a variation of the total energy with respect to some *trial function* which is taken as a superposition of basis functions within a finite, but appropriately chosen (many-electron) subspace. Usually, the choice of the basis must be made on the grounds of physical insight or previous experience; the many-electron basis functions are called configuration state functions (CSF) and are typically constructed as antisymmetrized products of one-particle functions. Clearly, the particular choice of these spin-orbital functions as well as of the CSF basis as a whole plays a crucial role in all CI computations and, eventually, decides which atomic states are selected and how well they can be approximated in such a basis. Below, we will restrict ourselves to jj-coupled CSF which are built on standard one-electron Dirac orbitals. Within such a framework, the known techniques of Racah's algebra can be applied to evaluate the (many-electron) Hamiltonian matrix.

The basic principles of relativistic atomic structure theory have been reviewed in detail by Grant [12,13] and elsewhere; these texts also include a number of *technical* elements which facilitate the computations. In the following discussion, therefore, we will only focus on a few selected topics to help understand the design of the RELCI program and how it differs from previous implementations. A key role in the set-up and diagonalization of Hamiltonian matrices is certainly played by the (relativistic) interaction, which has to be taken into account for each pair of electrons, as well as by the construction of the CSF basis. Both choices influence the evaluation of the matrix elements and, thus, the computations which need to be carried out in detail. Historically, many details of the relativistic atomic structure theory date far back to the work of Breit [14] for the electron–electron interaction and to Racah's introduction of spherical tensors [15].

2.1. Electron–electron interactions

In atomic physics, the interaction among each pair of electrons is typically divided into two parts, the (static) Coulomb repulsion

$$\frac{1}{r_{12}} \equiv \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{1}$$

and the so-called *Breit interaction* [14], which are often treated independently. The Breit interaction describes the relativistic corrections to the electronic motion due to magnetic and retardation effects. An effective operator for the Breit interaction can be derived from quantum electro-dynamics (QED) in perturbation theory with respect to the number of virtually exchanged photons [16,17]; in Coulomb gauge, for instance, the (transverse) Breit interaction is

$$b_{12} = \frac{\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2}{r_{12}} + (\boldsymbol{\alpha}_1 \cdot \boldsymbol{\nabla}_1)(\boldsymbol{\alpha}_2 \cdot \boldsymbol{\nabla}_2)\frac{\cos(\omega r_{12} - 1)}{\omega^2 r_{12}} \tag{2}$$

where $\omega = \frac{|\epsilon_1 - \epsilon_2|}{c}$ describes the difference in the one-particle energies. From this expression, also, the *frequency-independent* (and original) Breit operator

$$b_{12}^0 = -\frac{1}{2r_{12}}\left[\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + \frac{(\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})}{r_{12}^2}\right] \tag{3}$$

is obtained in the long-wavelength approximation, $\omega \to 0$. This zero-frequency approximation to the full transverse interaction neglects all contribution $\sim a^4 Z^3$ (and of higher order in αZ) but is well suited for most computations of many-electron atoms and ions since the explicit frequency-dependence of expression (2) usually gives rise to only (very) small corrections. When compared with missing correlation contributions, the frequency dependence is completely negligible for most open-shell configurations. Below, we will therefore use the term *Breit interaction* for both, expressions (2) and (3), and only specify the particular form if necessary, indeed.

In the frequency-independent form (3), moreover, the first term

$$b_{12}^{\mathrm{G}} = -\frac{\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2}{2r_{12}} \tag{4}$$

describes the current–current interaction of the moving electrons and is known in the literature as *Gaunt interaction*. For closed-shell atoms, this term yields about 90% of the total (relativistic) energy shifts to the atomic levels [18].

Although, up to the present, the relativistic operators (2)–(4) are mainly applied in first-order perturbation theory, they should be treated as an integral part of the electron–electron interaction

$$v_{12} = \frac{1}{r_{12}} + b_{12}, \tag{5}$$

i.e. *formally equivalent* to the static Coulomb repulsion. In the RELCI program, these relativistic contributions b_{12} to the electron–electron interaction can be incorporated in any of the given forms (2)–(4), or may also by omitted in the set-up of the Hamiltonian matrix if their influence is expected to be small. As introduced above, we will refer to these three operators as transverse Breit, frequency-independent Breit, or Gaunt interaction in further discussions and, usually, in addition to the—inherently assumed—Coulomb operator (1).

The evaluation and explicit computation of the electron–electron interaction matrix certainly requires the dominant effort in all atomic structure calculations. Therefore, the decomposition and implementation of the matrix elements to the operators (1)–(4) deserves particular care in any new implementation of a CI program. A clear simplification of the many-electron matrix elements is achieved if all the operators are represented in terms of spherical tensors [19]

$$g_{12} \equiv g(\mathbf{r}_1, \mathbf{r}_2) = \sum_L g_L(r_1, r_2) \big(\mathbf{T}^{(L)}(\theta_1, \phi_1) \cdot \mathbf{T}^{(L)}(\theta_2, \phi_2) \big) \tag{6}$$

which facilitate the analytic integration over all spin-angular variables. For a symmetric operator, i.e. $g_{12} = g_{21}$, then the matrix elements

$$\begin{aligned} \langle ab|g_{12}|cd\rangle &\equiv \big\langle n_a\kappa_a m_a(1), n_b\kappa_b m_b(2) \big| g_{12} \big| n_c\kappa_c m_c(1), n_d\kappa_d m_d(2) \big\rangle \\ &= \sum_{LM} (-1)^{L-M+j_a-m_a+j_b-m_b} \begin{pmatrix} j_a & L & j_c \\ -m_a & M & m_c \end{pmatrix} \begin{pmatrix} j_b & L & j_d \\ -m_b & -M & m_d \end{pmatrix} X^L(abcd) \end{aligned} \tag{7}$$

simply factorize into a sum of products where the (physical) interaction among the particles only occurs in the factors $X^L(abcd)$, the so-called *effective interaction strengths* of order L. The dependence of the matrix elements on the particular choice of the quantization axis, i.e. the magnetic quantum numbers, in contrast, arise only in the phase factor and the Wigner $3j$ symbols. In expression (7), $|a\rangle = |n_a\kappa_a m_a\rangle \equiv |n_a j_a l_a m_a\rangle$, $|b\rangle = |n_b\kappa_b m_b\rangle, \ldots$ denote one-particle states with definite angular momentum and parity as well as projection of the angular momentum. For the explicit form of $X^L(abcd)$ for the various interaction operators (2)–(4), we refer the reader to the literature. Here, we just note that this decomposition is essential for an efficient set-up of the Hamiltonian matrix. Moreover, Eq. (7) shows the *central role* which is played by the effective strengths $X^L(abcd)$. In order to incorporate, for example, the Gaunt interaction in addition to the Coulomb repulsion, we can simply write $X^L(abcd) = X^L_{\text{Coulomb}}(abcd) + X^L_{\text{Gaunt}}(abcd)$.

2.2. Relativistic Hamiltonians in atomic structure theory

As in nonrelativistic quantum theory, relativistic structure calculations are typically built on a Hamiltonian operator which describes a fixed number of particles, N. Hence, by starting from Dirac's theory and making use of the last subsection, we immediately arrive at either the *Dirac–Coulomb–Breit* Hamiltonian

$$H_{\text{DCB}} = \sum_i h_{\text{D}}(\mathbf{r}_i) + \sum_{i<j} \left(\frac{1}{r_{ij}} + b_{ij} \right) \tag{8}$$

or the *Dirac–Coulomb* Hamiltonian

$$H_{\text{DC}} = \sum_i h_{\text{D}}(\mathbf{r}_i) + \sum_{i<j} \frac{1}{r_{ij}} \tag{9}$$

if, in the latter case, the relativistic corrections to the static Coulomb repulsion are to be neglected. In both Hamiltonians,

$$h_{\mathrm{D}} = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta c^2 + V_{\mathrm{nuc}}(r) \tag{10}$$

is the one-electron Dirac operator which describes the kinetic energy of the electron and its interaction with the (external) nuclear potential $V_{\mathrm{nuc}}(r)$. The term b_{ij} in (8) can be either one of the expressions (2)–(4) where the particular choice has to be made on the grounds of physical arguments in all practical applications. Although the decision about the underlying Hamiltonian operator is often made on the basis of the nuclear charge or the charge state of the system, it may also depend on the shell structure and the properties which are to be investigated with these wave functions. Apart from the computation of the energies and wavefunctions, the same operators also occur in Auger processes or in the study of the electron-impact excitation and ionization. A careful notation for the interaction operators may therefore help implement further excitation and decay properties in the framework of the RATIP package.

Note, however, that the accuracy of all computations does not only depend on the choice of the interaction operator but, and often to a much larger extent, also on limitations in the many-electron basis. For a given wave function expansion, the influences of these two approximations are hard to discuss separately.

Not much need to be said about the properties of the Hamiltonian operators (8) and (9), i.e. about a discussion which is better known by the keywords *Brown–Ravenhall* effect or *continuum dissolution*. For the present implementation of the corresponding Hamiltonian matrices in RELCI it is sufficient to *assume* that, in the construction of the CSF basis, an appropriate set of one-electron functions has already been generated *prior* to the start of the program. Then, all what remains is the evaluation and diagonalization of the (many-electron) Hamiltonian matrix in order to obtain a proper representation of the atomic states.

2.3. Decomposition of Hamiltonian matrix elements

In the configuration interaction method, an atomic state is approximated by a superposition of configuration state functions

$$\big|\psi_\alpha(PJM)\big\rangle = \sum_r^{n_c} c_r(\alpha)|\gamma_r PJM\rangle. \tag{11}$$

To emphasize the *equivalence* of this method with the multiconfiguration Dirac–Fock model, once the active set of one-electron orbitals was fixed, we use here the same notation as given in the literature about the GRASP program [2,13]. From the symmetry of free atoms with respect to a rotation or inversion of coordinates it is clear that the Hamiltonian matrix is always block-diagonal in the total angular momentum and parity quantum numbers (PJM). For large-scale computations, therefore, ansatz (11) can be restricted to include only those basis functions which have the same overall symmetry.

A representation of an atomic state ψ_α in the given CSF basis, i.e. the mixing coefficients $\mathbf{c}(\alpha) = (c_1(\alpha), c_2(\alpha), \ldots, c_{n_c}(\alpha))$, is obtained by solving the secular equation

$$\det\big(\mathbf{H} - E_\alpha^{(n_c)}\mathbf{I}\big) = 0, \tag{12}$$

where $E_\alpha(PJ)$ denotes the eigenvalue and

$$\mathbf{H} = (H_{rs}) = \big(\langle\gamma_r PJM|H|\gamma_s \bar{P}\bar{J}\bar{M}\rangle \delta_{P\bar{P}}\delta_{J\bar{J}}\delta_{M\bar{M}}\big) \tag{13}$$

the Hamiltonian matrix. Note that the block symmetry of this matrix (13) is independent of the particular choice of the electron–electron interaction in the Hamiltonian as discussed earlier. In addition, since this matrix is real and symmetric, all atomic states are orthogonal for $E_\alpha \neq E_\beta$ or can be chosen in this way for $E_\alpha = E_\beta$.

Of course, the set-up and decomposition of the Hamiltonian matrix elements [cf. Eqs. (8) and (9)] eventually depend on how the many-particle basis is constructed from the one-particle functions. As before, we assume

jj-coupled CSF for which the angular integration can be carried out analytically using the techniques of Racah's algebra. For scalar two-particle operators (like all of the electron–electron interaction operators), a new implementation of the analytic integration in the framework of the RATIP package has been presented recently [11] and is internally used also by RELCI.

The analytic integration over the angular variables of all electrons gives rise to a decomposition of the Hamiltonian matrix elements in the form

$$H_{rs} = \sum_{ab} t^{o}_{rs}(ab)\langle a\|h_{\mathrm{D}}\|b\rangle + \sum_{L}\sum_{abcd} v^{L}_{rs}(abcd)X^{L}(abcd), \tag{14}$$

where $t^{o}_{rs}(ab)$ and $v^{L}_{rs}(abcd)$ are one- and two-particle (scalar) angular coefficients and the $X^{L}(abcd)$ describe the effective interaction strengths. Similar to Eq. (7), we use again an abbreviation of the quantum numbers $a = (n_a, \kappa_a)$, $b = (n_b, \kappa_b), \ldots$ in order to describe the different subshells of equivalent electrons in the construction of the basis. The reduced matrix element in the first term of (14)

$$\begin{aligned}\langle a\|h_{\mathrm{D}}\|b\rangle \;=\; \delta_{\kappa_a\kappa_b}\int_0^\infty \mathrm{d}r\Big[cQ_a\Big(\frac{\mathrm{d}}{\mathrm{d}r}+\frac{\kappa_a}{r}\Big)P_b + cP_a\Big(-\frac{\mathrm{d}}{\mathrm{d}r}+\frac{\kappa_a}{r}\Big)Q_b \\ -2c^2Q_aQ_b + V_{\mathrm{nuc}}(r)(P_aP_b+Q_aQ_b)\Big]\end{aligned} \tag{15}$$

can be considered as the one-particle *analogue* to the effective interaction strength [cf. Eq. (7)]. These reduced matrix elements describe the kinetic and potential energy in the (static) field of the nucleus and may only arise for those matrix elements of the Hamiltonian for which the occupation of the CSF (r, s) on the left- and right-hand side differ by less than two. In most computations, moreover, the (multiple) summation over all possible subshells $a, b, \ldots$ and ranks L is typically replaced by a single index which runs through all non-vanishing angular coefficients of the corresponding type. Note that the ranks of the interaction strengths in (14) depend, of course, on the particular choice of the electron–electron interaction.

The concept of the effective interaction strength has been utilized strictly throughout the present implementation. For the further development of the RATIP package, this concept will facilitate to consider also other atomic and collision properties which are affected by the interaction among the electrons. When compared with the previous definition of the radial integrals in the GRASP program, a careful use of the interaction strength, i.e. of reduced matrix elements, helps us with a simpler implementation and maintenance of the code. Below, we make use even further of this concept by *incorporating* the contributions from the vacuum and the specific mass polarization (in first order) to these effective strengths.

The symmetries of the Hamiltonian matrix (13) are sufficient to understand the implementation of RELCI below. Once the (one- and two-particle) angular coefficients have been determined for a given pair of CSF, we just need to calculate the effective strengths as appropriate for the selected type of interaction among the electrons. For each of the two-particle interaction operators (1)–(4), there is a corresponding effective strength parameter $X^{L}(abcd)$ which have been discussed in the literature [20]. For the Coulomb repulsion, for example,

$$\begin{aligned}X^{L}_{\mathrm{Coulomb}}(abcd) \;=\; &\delta(j_a, j_c, L)\delta(j_b, j_d, L)\Pi^{e}(\kappa_a, \kappa_c, L)\Pi^{e}(\kappa_b, \kappa_d, L) \\ &\times (-1)^{L}\big\langle\kappa_a\big\|\mathbf{C}^{(L)}\big\|\kappa_c\big\rangle\big\langle\kappa_b\big\|\mathbf{C}^{(L)}\big\|\kappa_d\big\rangle R^{L}(abcd)\end{aligned} \tag{16}$$

where the *triangular* $\delta(j_a, j_b, j_c)$ ensures the proper coupling of the angular momenta and the even-parity coefficient

$$\Pi^{e}(\kappa_a, \kappa_b, L) = \begin{cases} 1 & \text{if } l_a + l_b + L \text{ even,} \\ 0 & \text{otherwise} \end{cases} \tag{17}$$

reflects the selection rules for the Coulomb interaction. Finally, $R^L(abcd)$ denotes the relativistic Slater integral [13]. Similar, although more elaborate expressions also arise for the other interactions (2)–(4), utilizing a representation of these operators in terms of spherical tensors [21]. When compared to the Coulomb case, however, different decompositions of the operators lead to different angular momenta and parity selection rules.

The effective strengths $X^L(abcd)$ are the *building blocks* in the computation of the Hamiltonian matrix elements. For a moderate number of (radial) orbital functions, they can easily be stored and kept throughout the computation once they have been calculated. Details about the storage management for these interaction strengths in RELCI and its internal implementation will be explained below. An analysis of the vacuum polarization (VP) and (specific) mass polarization (SMS) shows, moreover, that their contributions can be *added* also to the *effective interaction strength* in rather much the same way

$$\langle a \| h_{\mathrm{D}}^{\text{effective}} \| b \rangle = \langle a \| h_{\mathrm{D}} \| b \rangle + x_{\mathrm{VP}}(ab), \tag{18}$$

$$X^{L,\text{effective}}(abcd) = X^L(abcd) + X^L_{\mathrm{SMS}}(abcd). \tag{19}$$

In RELCI, the contributions from these two corrections are incorporated into the Hamiltonian matrix following lines similar to GRASP92 [3].

To summarize the set-up of the Hamiltonian matrix, let us recall the main two steps in the computation of the individual matrix elements. First, we generate the (pure) angular coefficients for each pair of CSF by a call to the ANCO component [11]. For these coefficients, then, the corresponding one- and two-particle effective strengths are either read out from the internal storage or they are re-calculated including all the interactions as specified by the present run of the program. A similar procedure could be followed for calculating Auger rates and electron-impact cross sections if appropriate continuum functions are available. The great advantage of such a decomposition is that it simplifies the maintenance of the program and can easily be transferred to the calculation of many other atomic properties.

2.4. QED estimates from a hydrogenic model

The dominant radiative corrections to the level structure of free atoms arise from the self-energy of the electrons and the polarization of the vacuum due to the external nuclear field. These two QED contributions to the level and transition energies of atoms and ions are often comparable in size with the (relativistic) Breit interaction, particularly if inner-shell electrons are involved in some atomic process. The effect of the vacuum polarization can (at least in lowest order) be represented in terms of a Uehling potential [22] and has been included in relativistic structure calculations for many years now. As mentioned above, it *contributes* to the one-particle effective strengths $\langle a \| h_{\mathrm{D}}^{\text{effective}} \| b \rangle$ in (18) and can be taken into account in RELCI—if specified for the present run of the program.

The ab initio computation of the self-energy, in contrast, requires even in lowest order in αZ a considerably larger effort. So far, such computations have been carried out only for hydrogen-like ions and for a few selected levels in the helium isoelectronic sequence. For many-electron atoms and ions, the (total) self-energy contributions are usually estimated from tabulations which are available for the hydrogen-like ions. Different methods have been proposed and applied in the past to determine an *effective* nuclear charge, Z_{eff}, to interpolate these data for the individual subshells of a many-electron system. In such a procedure, the total self-energy shift is taken as the sum of the effective one-particle contributions for the K- and L-shell electrons and by using an n^{-3} scaling rule for the electrons in higher shells.

An alternative method to *estimate* the one-particle contributions to the self-energy in many-electron atoms has been suggested by Kim [10]. This method follows the idea that the dominant part of the self-energy *arises inside or very close to the nucleus,* i.e. within a sphere of, say, 40...60 fm which, in fact, includes only a tiny part of the total electron density. An estimate of the self-energy of inner-shell electrons is therefore obtained by multiplying the hydrogen-like self-energy shift for a point nucleus with the corresponding charge ratio (inside such a sphere) as obtained from many-electron calculations. For hydrogen-like ions with a point nucleus, tabulations of the electron self-energy have been listed by Mohr [23] for $1s$, $2s$, and $2p$ orbitals and by Mohr and Kim [24] for ns, np, and nd $(n = 3, 4, 5)$ orbitals.

The fraction of the partial charge inside such a small sphere mainly reflects the screening of the nuclear charge due to the modified potential of a realistic (extended) nuclear model and the influence of the $N - 1$ other electrons. For most medium and heavy atoms and ions, Kim's method yields equivalent or even (much) better results when compared with previous methods of estimating an effective charge for the various (sub-)shells from many-electron calculations. Deviations from previous estimates arise, in particular, for rather heavy elements and for inner-shell transitions. In this case, the self-energy estimates from our present implementation were found to lead to better agreement with experiment. For large CI expansions, moreover, the present method has been found faster and more stable.

The self-energy contribution shifts the total level energies according to the occupation of the individual subshells. In the given model, these contributions are not part of any *effective* Hamiltonian and, hence, should not be incorporated into the diagonalization of the matrix as has been implemented in an earlier version of GRASP [2]. To distinguish these QED estimates from the outcome of the many-electron computations, moreover, the total energies of the selected levels are typically displayed twice in RELCI, without and with these estimates included (if requested by the user). But although the self-energy corrections do not enter the representation of the wave functions, they can be *added* to the total energies also in the `.mix` file (see below) in order to facilitate the computation of other properties which depend explicitly on the transition energies. Since all radiative corrections in RELCI are always estimates, they should be handled carefully, in particular if small level splittings are to be discussed.

3. Program structure and implementation

3.1. The RATIP package

RELCI is designed as a new component of the RATIP package [25,26] which has been developed in order to exploit MDCF wave functions in the calculation of *relativistic atomic transition and ionization properties.* Over the years, the range of possible applications of this package has been enlarged substantially to include the autoionization of atoms and ions, their interaction with the radiation field, lifetime interference effects between radiative and nonradiative processes as well as studies on the angular properties of the emitted electrons and photons. In a large number of case studies, RATIP helped analyze and interpret a variety of spectra and experiments. In its current design, the RATIP package is built on the (relativistic) wave functions of GRASP92, an implementation of the MCDF model as described above. Since, in this model, the wave function generation can be built on either the Dirac–Coulomb (9) or Dirac–Coulomb–Breit Hamiltonians (8), both packages—GRASP92 and RATIP—support the incorporation of all dominant *physical effects* for (nearly) neutral atoms as well as for multiple and highly-charged ions. This includes electron–electron correlations, relativistic effects and, if the atom or ion undergoes a transition, the rearrangement of the electron density. It is one of the advantage of RATIP that these effects can be treated consistently within the same framework.

The present design of RATIP as an *open environment* will facilitate the implementation of new and efficient concepts and developments in atomic structure theory in the future. At present, the whole package is based on about 25 modules which serve for a number of purposes, not all of them being yet of interest for the user. Apart from the computation and diagonalization of (very) large Hamiltonian matrices as described here, the published version of RATIP supports (i) the transformation of symmetry-adapted functions from GRASP92 into a determinant basis [26], (ii) the computation of transition probabilities and (radiative) lifetimes [4], the calculation of (iii) reduced coefficients, matrix elements [27] and (iv) angular coefficients [11] as well as (v) a toolbox to support a number of small tasks. Further components (which were already part of an older version of RATIP) will support (vi) the generation of continuum orbitals, (vii) the calculation of Auger rates and angular distribution parameters, and

(viii) photoionization cross sections; these additional components are presently adapted to the new standard and will be released soon. In line with this step-wise development of the RATIP environment, below we distribute those modules which are needed for RELCI and all previously distributed components. The present distribution also includes a few corrections to the previous version.

3.2. Internal set-up and diagonalization of the Hamiltonian matrix

Section 2.3 showed that the Hamiltonian matrix exhibits a block structure, if constructed from a symmetry-adapted basis. Hence, the (total) energies and eigenvectors of the Hamiltonian can be found by diagonalizing these symmetry blocks separately. In practice, moreover, one may calculate just a single block of the Hamiltonian matrix in each run, even though this ‘external splitting’ of a given computation does not always fit to the *requirements of the user.* For large matrices, in addition, only a subset of the eigenvectors is often required which, consequently, are better determined by an iterative procedure, instead of the diagonalization of the full matrix. For such a procedure, a useful and efficient algorithm is due to Davidson [28] which helps determine selected solutions for matrices of a dimension $n \simeq 10{,}000\ldots 100{,}000$ or even larger. In RELCI, we support both ways, the full diagonalization by means of the LAPACK routine DSPEVX as well as Davidson’s method, depending on the size of the matrix. The decision is made internally due to the (global integer) parameter `Hamiltonian_fullmatrix` which is defined in the header of the module `rabs_hamiltonian`. This parameter is currently initialized with a value 500. For utilizing Davidsons algorithm in RELCI, we use the implementation by Stathopoulos and Froese Fischer [29] which is presently accessible (to us) only in Fortran 77; these procedures will be replaced in the future as an upgrade of Davidson’s method (in Fortran 90/95) becomes available.

In the following, we briefly explain the internal set-up and storage management of the Hamiltonian matrix. In course of the computation, the symmetry of the given CSF basis is utilized by first analyzing its block structure at the beginning of the execution. To this end, the information about the symmetry blocks of the present run are collected in an array of type

```
type, public :: hamiltonian_block
integer(kind=i1b) :: totalJ
character(len=1) :: parity
integer :: nocsf
integer, dimension(:), pointer :: csf_ndx
real(kind=dp), dimension(:), pointer :: eigenvalue
real(kind=dp), dimension(:,:), pointer :: eigenvector
end type hamiltonian_block
```

which contains, apart from the overall symmetry J^P, the number of CSF in these blocks as well as their indices with respect to the original expansion (11) in the `.csl` file. Two additional (pointer) arrays in this data structure are ‘defined’, moreover, in order to keep the required set of eigenvalues and eigenvectors of a particular block until they can be ordered together for all different blocks in the computation.

In standard applications of the RELCI program, one typically wishes to determine a number of low-lying levels, say the lowest 20 levels of a given expansion, whose sequence and symmetries (J^P) are not known *prior* to the computation. Indeed, for a ‘mixed’ wave function expansion, not much is known of which and how many solutions of a particular block J^P are required. In the present version of RELCI, the pointer arrays `eigenvalue` and `eigenvector` in the derived `type(hamiltonian_block)` are therefore used to store the maximal number of possible solutions, i.e. all 20 solutions in the example above. The desired set of (total) energies and mixing coefficients are determined only afterwards when all the symmetry blocks of the Hamiltonian matrix have been diagonalized.

In dealing with large matrices, the decomposition and computation of the Hamiltonian matrix elements is typically the most time-consuming part. To a large extent, this arises from the (angular) integration over the $3N$

spin-angular coordinates, if N is the number of electrons in the basis. This angular integration has to be carried out for each pair of CSF separately. In RELCI, all angular coefficients are now obtained from the ANCO component [11,30] of the RATIP program which refer directly to the one- and two-particle effective strengths in (18) and (19), respectively. Owing to this decomposition of the many-electron matrix elements into *pure angular* coefficients and effective strengths, the *same set of coefficients* can be used to generate the Dirac–Coulomb, Dirac–Gaunt, or Dirac–Coulomb–Breit matrices.

The decomposition of the Hamiltonian matrix into pure coefficients and effective interactions has another advantage also for the maintenance and the further development of the RATIP package. Other (types of) *interactions* can be added without that large modifications of the code become necessary. Each contribution to the Hamiltonian matrix is internally *activated* or *deactivated* by a logical flag like, for instance, `hamiltonian_XL_coulomb,hamiltonian_XL_gaunt,...`. The default values for these switches are defined in the header of the module `rabs_hamiltonian`; they can be modified also interactively. The computation and the storage management of the individual contributions to the Hamiltonian are controlled, in particular, by the two module procedures `hamiltonian_T0_storage` for the one-particle effective contributions and `hamiltonian_XL_storage` for the two-particle effective strengths, respectively. These two procedures also maintain the internal storage, if a part or all of the effective strengths ought to be kept during the execution.

The computation of the Hamiltonian matrix does not only require the main part of the CPU time but may demand also a large amount of memory. Even for a blockwise computation of the Hamiltonian matrix, the size of an individual block may easily use all available memory, for example. In order to support as many applications as possible, we therefore distinguish (and implemented) three *computational modes* with regard to the handling and storage of the Hamiltonian matrix. In the default mode, the internal memory but no separate disc space is utilized, apart from the final printout. On present-day computers, matrices of dimension $n_c \lesssim 20{,}000$ can be handled in this mode, possibly, by using some of the swap space. This mode also ensures the fastest execution of the program, since no access to external storage media is required. However, since the amount of the available RAM (random access memory) does not only depend on the hardware but also on competitive processes, which are started and executed dynamically on most computers, the maximal dimension (of a successful matrix diagonalization) is difficult to decide in advance. Therefore, no attempt has been made to switch the internal mode automatically to a—secondly supported—*disc mode* in which the Hamiltonian matrix elements of the individual blocks are written sequentially on disc while they are generated. Although this mode requires less RAM memory, of course, the user has to make sure that enough disc space is available during the execution of RELCI; note that this mode is slower by about a factor of 1.5…2.5 on a standard PC if compared with the default. In typical applications of RELCI, the required RAM or disc space (in MB) scales approximately with $n_s^2/10^6$ where n_s is the number of CSF in the largest symmetry block J^P of the Hamiltonian matrix. In the disc mode, moreover, the individual columns of the Hamiltonian matrix are later read in from the file as they are needed in course of the diagonalization. A third computational mode (*direct mode*), finally, allows for the *direct* diagonalization of the Hamiltonian where all matrix element are calculated just *on fly*, each time they are needed. Because of the ‘costs’ of the angular integration, this mode is (currently) not compatible with the other modes with regard to the CPU time but might become of interest for parallel applications in the future. This should be true particularly on distributed environments for which communications between different processes often result in a delay much larger than would be caused by the recalculation of the matrix elements every time they are needed.

Even though we provide several modes for the computation of the Hamiltonian matrix, a *restart* of the program from a previously aborted run is no longer supported. This decision was made on the basis of our experience with large-scale computations, namely that a restart feature became less frequently required as the codes were moved to the workstation or PC world. For such an environment, typically, no (predefined) time limits apply. From the three computational modes as described above, only the disc mode would allow for a restart of RELCI; however, for the price that an additional interface file is needed to store the eigenvalues and vectors from the already diagonalized blocks between the different runs of the program.

3.3. Interactive control of execution and output of the program

Like the other components of RATIP, the RELCI program is controlled interactively at the beginning of the execution. Beside of some mandatory input, which specifies the CSF basis as well as the (energy) units and the output format, we provide an *optional* control about the choice of the Hamiltonian matrix and the computational mode. In the next section, we display a typical input dialog as been used for the test case below. The *optional* part of the input is executed only when the question *“Modify the default set-up and printout of the program?”* is answered by y(es).

Of course, the input must describe a valid CSF basis in terms of a configuration symmetry list file (`.csl`) and a set of radial orbitals (`.rwf`) from GRASP92. Other information about the nuclear potential is obtained from the (`.iso`) isotope data file. These three files from the GRASP92 environment together contain all that is necessary to set up the (default) Hamiltonian matrix. To simplify the application for large wave function expansions, moreover, we recently developed the UTILITIES of the RATIP package which support about 16 frequently required tasks. These tasks include, for example, the fast merging of—two or more—`.csl` lists or the elimination of certain classes of virtual excitations which may contribute less likely to the atomic levels of interest.

In the present distribution, the default interaction of RELCI include the Dirac–Coulomb–Breit Hamiltonian in the low-frequency limit $\omega \to 0$, a choice which can be overwritten interactively. Fig. 1 shows a part of this *optional* dialog which can be invoked in order to specify the ‘interactions’ differently. Alternatively, the default execution of RELCI can be modified by some logical switches in the header of the module `rabs_hamiltonian`; they are re-initialized always at the beginning of the program. In contrast to RCI92 of the GRASP92 program, however, the radial integrals to the frequency-independent Breit interaction are calculated separately from the full transverse interaction in RELCI. This separation helps save time in the execution of the program and, hence, appears more suitable for most neutral atoms and multiple-charged ions for which the frequency-dependent parts of the interaction are known to be negligible. The use of the frequency-independent Gaunt interaction, in addition to the Coulomb term, may help, moreover, to study the gauge dependence of the relativistic electron–electron interaction.

A summary about the set-up and the diagonalization of the Hamiltonian matrix is written to the RELCI (`.sum`) summary file. This file contains the date and time of the execution, information about the orbital functions and, of course, the results from the diagonalization. This summary file also displays a short statistics on the computation, i.e. about the number of angular and radial integrals and how many of them have been *re-used* from the internal storage management in course of the computation. For the selected levels, the summary file tabulates the total energies as well as the excitation energies and levels splittings. The selected eigenvalues and eigenvectors are written unformatted to the RELCI (`.mix`) mixing coefficient file for which we utilize the same format as in the GRASP92 environment. But apart from this original file format of GRASP92, we also support a formatted output if the logical switch `relci_use_formatted_mix_file` is set to `.true`, in the header of `rabs_Relci`. This formatted version not only helps for developing the code but became necessary also because not all Fortran 90/95 compilers do support the—rather long—records of RCI92 as they may arise in large-scale applications. Moreover, the formatted version of the `.mix` file is consistent also with other components of RATIP like, for example, CESD99 [26] or AUGER.

In the RELCI summary file, the first tabulation of the total energies and levels splitting always list the outcome of the diagonalization, independent of any self-energy estimates. If such estimates were requested, they are *added* to the energies from the diagonalization of the matrix and are re-written to the summary file. In order to be consistent with GRASP92, these self-energy estimates are not incorporated (by default) into the total energies of the mixing coefficient file; this option must be selected separately in the input but has been found useful for studying inner-shell transitions for medium and heavy atoms.

```
 RELCI: Set-up and diagonalization of a relativistic CI matrix including
  Breit interactions and QED estimates (Fortran 90 version)
  (C) Copyright by S Fritzsche and others, Kassel (2001).
 Generate debug printout ?
n
 Enter a file name for the  relci.sum  file:
FeX-e1-3sq4sd-relci.sum
 Enter the name of the configuration symmetry list file:
FeX-e1-3sq4sd.csl
 Loading configuration symmetry list file ...
  There are  16  relativistic subshells;
  there are  3375  relativistic CSFs;
  ... load complete.
 Enter the name of the isotope data file:
isodat26
 loading isotope data file ...
  ... load complete;
 Modify default set-up and printout of the program ?
y
 Include contributions from the Coulomb interaction ?
y
 Include contributions of the transverse Breit interaction ?
n
 Include contributions of the frequency-independent Breit interaction ?
y
 Include vacuum polarization contributions to H ?
y
 Include normal mass shift contributions to H ?
n
 Include specific mass shift contributions to H ?
n
 Estimate contributions from self-energy ?
y
 Add self-energy estimates to the total energies in the .mix output file ?
  This can be useful in the computation of transition energies.
n
 Store the effective interaction strengths in memory ?
  This should always be true for a on--fly calculation of the Hamiltonian matrix.
y
 Precalculate and keep Hamiltonian matrix in memory ?
y
 Which units are to be used to print the results ?
     A       : Angstrom;
     eV      : electron volts;
     Hartree : Hartree atomic units;
     Hz      : Hertz;
     Kayser  : [cm**(-1)];
eV
  .
  .
 Enter the name of the GRASP92 Radial WaveFunction File:
FeX-e1-3sq4sd.out
  ... load complete;
 Enter a file name for the  relci.mix  file:
FeX-e1-3sq4sd-relci.mix
 Enter the serial number(s) of the level(s) to be calculated;
  e.g. 1 3 4  7 - 20  48  69 - 85;
1 - 7
```

Fig. 1. Interactive dialog for RELCI.

3.4. Distribution and installation of the program

Over the years, the number of modules which belong to the RATIP package has been increased considerably. There are now a total of about 25–30 modules which support the computation of different properties. However, not all of them are required at the present version of the RATIP program. Together with a few modules, which were particularly designed for RELCI, we distribute the source code for the components ANCO, CESD99, RCFP, REOS99, and UTILITIES. They are contained in the `ratip` root directory which, in addition, includes the two libraries `dvdson` and `lapack`. This root directory also comprises several makefiles for generating the executables as well as test suites for the different components. As previously, the command `make-f make-component` generates the executable of the corresponding component (i.e. `xanco, xcesd99, xrcfp,...`).

To enlarge the portability of the program, the `ratip` root also provides the user with the script file `make-environment`. This script is used to define a number of global variables for the compilation and linkage of the program. It saves the user adopting each makefile independently, for instance, if the local architecture is to be changed or if another compiler (or flags) is to be used while the structure of the makefiles still remains simple. In fact, the script `make-environment` only contains a few lines which have to be adopted to the local environment; they are prepared for the two operating systems AIX and LINUX. By running the command `source make-environment` all information from this file is made available to the system. Apart from the two libraries `dvdson` and `lapack` (which we expect to replace in the future), no further libraries nor the adaptation of any dimension is required to run the program. The present version of RATIP has been found easily portable to different platforms like IBM RS/6000, SUN OS, or to the PC world.

For each component of the RATIP package, we typically provide a test suite in the subdirectory `test-component`. The directory `test-relci` in the `ratip` root, for instance, contains all required input and output files for the example as described in the following section. These test suites are designed with the intention of providing the user with both a quick test of the installation as well as a demonstration for each component.

The size of the RATIP package makes it impossible for us to explain each procedure individually. There are now overall more than 400 subroutines which are arranged within a hierarchy of modules according to their purpose and the context in which they occur. For other components like AUGER, PHOTO, or others which are not yet distributed, further modules and procedures are still under development. In general, each module collects the procedures in alphabetic order; they are briefly explained in the header of the module. Further information about the methods, data structures, etc. and their implementation can be found in many *in-line* comments in the headers of the individual procedures or directly inside of the source code.

4. Test case: The level structure of Fe^{9+} ions

Recent space observatories in astrophysics like the Solar and Heliospheric Observatory (*SOHO*) or the Far Ultraviolet Spectroscopic Explorer (*FUSE*) have renewed the interest on multiple and highly-charged ions. In the extreme ultra-violet (EUV) range of the spectra, for instance, many of the spectroscopically observed lines belong to the iron-group elements owing to their high abundance in a variety of astrophysical objects. Till today, however, many of these lines remained unclassified because reliable theoretical predictions are not available yet; clearly, such calculations must incorporate relativistic and correlation effects consistently within the same framework. Therefore, in order to demonstrate RELCI'S capabilities for this particular domain of relativistic computations (and to test the program), here we consider the level structure of Fe^{9+} ions which, in spectroscopic notation, give rise to the spectrum Fe X. But, although a number of theoretical investigation have been carried out for this spectrum previously [32], even a recent (semi-empirical) analysis by Deb and Tayal [33] still led to excitation energies with an accuracy of only 1–3%, i.e. with deviations of up to 20,000 cm^{-1} from evaluated data [35] for the upper levels of the $3s^2 3p^4 3d$ configuration. With the present example, we show that pretty large-scale ab initio computations with GRASP92 and RELCI now help improve such predictions for (low-lying) level structures considerably.

For the present example, all input files (and the corresponding output for later comparison) are distributed together with the program in the sub-directory `test-relci`. These files provide both a description of the nuclear model (`isodat26`) as well as the wave function expansions which are required to compute the total energies of the $3s^23p^5$, $J = 1/2, 3/2$ ground-state levels and the even-parity $3s3p^6$, $3s^23p^43d$, $J = 1/2$ excited levels. In `test-relci`, these expansions are given in terms of the configuration symmetry list files `FeX-ground-3sq4sd.csl` and `FeX-e1-3sq4sd.csl` as well as the corresponding radial orbital files `FeX-ground-3sq4sd.out` and `FeX-e1-3sq4sd.out`, respectively. In order to keep these test calculations feasible, however, we just incorporate quadruple excitations of all seven valence electrons within the $3l$ subshells as well as single and double excitation into the $4l$ shells in the wave function expansion. This limitation results in a total of 1639 CSF for the two $^2P_{1/2,3/2}$ ground-state levels and of 3375 CSF for the $J = 1/2$ excited levels. Further studies with much enlarged wave function expansions, including single and double excitations into the $5l$ and $6l$ shells, have been carried out recently [31,34], along with a detailed analysis of the spectrum. Such computations easily arrive at expansions of several ten thousand CSF or more and, hence, just emphasize the need of an efficient set-up and diagonalization of the Hamiltonian matrices.

In the following, we explain the input (Fig. 1) and the calculations for the seven $3s3p^6$, $3s^23p^43d$ $J = 1/2$ excited levels; similar calculations will have to be carried out for the two ground-state levels, if excitation energies ought to be derived and compared with experiment. In addition to the mandatory input, Fig. 1 displays parts of the optional dialog which helps select and modify the default interactions in the Hamiltonian matrix, the use of the internal storage, and the computational mode. In the present computations, we incorporate the frequency-independent Breit interaction and the vacuum polarization in addition to the Coulomb repulsion. We also select the option of self-energy estimates. This optional part of the dialog was implemented to overwrite the logical switches as defined in the header of `rabs_relci`; it later returns with the question *Which units are to be used to print the results?* back to the standard dialog to prompt for the radial orbital (`.out`) and the mixing coefficient (`.mix`) files. Finally, we select the seven lowest levels 1–7 for diagonalization.

The results of this run are written to the `FeX-e1-3sq4sd-relci.sum` and `FeX-e1-3sq4isd-relci.mix` files. These files are included for comparison also in the subdirectory `test_relci` where we used the formatted file format for the mixing coefficients. Other output, as shown below in the TEST RUN OUTPUT, is printed to the standard stream, including a short report about the current status of the program as well as the total and excitation energies, relative to the lowest. All of these energies agree to 8–10 figures with a corresponding run of the RCI92 component of GRASP92. In course of the set-up of the Hamiltonian, a single line is printed each time that 10^6 matrix elements (as default) have been calculated; this helps the user to estimate the total CPU time quite early at the beginning of the execution. Since the self-energy shifts are to be estimated in our test example, a second tabulation of the total energies, level splittings and excitation energies is printed to the standard screen; for valence-shell excitations of multiple-charged Fe^{9+} ions, however, these energy shift are completely negligible when compared with omitted correlations.

As well as for the level splitting among the low-lying $3s3p^6$, $3s^23p^43d$, $J = 1/2$ levels, comparison with evaluated data from the NIST Spectroscopic Database [35] can be made, for instance, for the excitation energies from the $3s^23p^5$, $J = 3/2$ ground state. To this end, similar computations as in our example above have to be carried out for the ground-state levels. Since excitation energies are obtained simply by subtracting the total energies, the same *choice of interactions* should always be considered if independent computations are performed. In the directory `test_relci`, we report results for both the $J = 1/2$ excited and the $3s^23p^5$, $J = 1/2, 3/2$ ground states.

5. Run-time comparison with RCI92

Our example from the last section shows how fast the size of the wave function expansions increase and, hence, how important an efficient diagonalization of large matrices is. Wave functions of several ten or even hundred

Table 1
Run-time comparison (in minutes) between RELCI and RCI92 for different sizes of wave function expansions. See text for an explanation of the various approximations. All computations include the Coulomb "plus" the frequency-independent Breit interaction; the results agree to within 10–12 figures for different computational modes of RELCI and within 8–10 figures when compared with RCI92. For RELCI, two computational modes are compared: (a) to keep the Hamiltonian in RAM memory and (b) to use disc storage for the matrix. Computations were carried out on a 550 MHz Pentium II standard PC. In our implementation, the RCI92 program failed to calculate the 4SDTQ approximation due to a bug in the angular components

Approximation	Number of CSF n_c	RELCI (a) RAM	RELCI (b) Disc	RCI92
$3s^2 3p^5$, $J = 1/2, 3/2$ ground-state levels				
4SD	1211	1	2	4
4SDT	14266	30	40	153
4SDTQ	33093	172	242	–
5SD	4326	11	14	35
$3s3p^6$, $3s^2 3p^4 3d$, $J = 1/2$ excited levels				
4SD	3227	6	10	39
4SDT	24399	158	233	674
5SD	13739	72	100	281

thousand CSF are feasible today but require, apart from efficient computer resources, powerful and flexible codes. To exhibit RELCI's gain in CPU time, Table 1 displays a run-time comparison with the RCI92 component from GRASP92 [3]. Again, we consider the level structure of Fe^{9+} ions but now in a series of different approximations, including single, double, triple, and quadruple excitations into different approximations. A notation like 4SDT, for instance, implies wave function expansions with single (S), double (D), and triple (T) excitations within the $4l$ subshells. For this run-time comparison, computations have been carried out for the two $J = 1/2, 3/2$ ground-state levels and the $J = 1/2$ excited levels by starting from the $3s^2 3p^5$ and $3s3p^6$, $3s^2 3p^4 3d$ *reference* configurations, respectively. As seen from column 2 of this table, the number of CSF, n_c, increases very rapidly. For RELCI, moreover, the time requirements of two different computational modes are shown. All calculations have been performed by means of a 550 MHz Pentium II processor.

Table 1 shows a clear gain in efficiently for RELCI when compared with RCI92 from GRASP92. This has been achieved mainly for two reasons: (i) the implementation of the new angular integration scheme which led to the component ANCO [1] and (ii) the revised decomposition and improved storage management of the Hamiltonian matrix as explained above. Both improvements accelerate the computation by a factor of about 2...4, resulting in a total gain of 3...8. Moreover, when the disc mode of RELCI is compared to the default mode, which makes use of the internal RAM, the latter one is faster by a factor ∼1.5...2.5. In all cases, the CPU time scales approximately with n_c^2 or even with a slightly higher power in n_c if very large matrices or many open shells are involved in the computations.

6. Summary

The recent development of tunable lasers and synchrotron radiation sources has renewed the interest in studying atoms and ions with an open-shell structure. Today, open p- and d-shell elements can be manipulated almost as easily as s-shell elements (the alkaline metals) two decades ago. To provide useful predictions for such complex systems, electron–electron correlations and relativistic effects must be treated consistently within the same program environment. With the development of RELCI, a significant step has been made forward which help extent the application of the GRASP92 and RATIP packages. By utilizing modern concepts for the angular integration and the set-up of the Hamiltonian matrix in RELCI, we are able to provide a code which is suitable for large-scale applications. The flexible choice of the *interactions* in the Hamiltonian matrix, moreover, may facilitate further studies not only with regard to the level structure of open-shell atoms and ions but also on their excitation and decay dynamics.

The implementation of RELCI as part of the RATIP package shows how new components will be appended to the code. Two other components which are currently adapted to the present standard of RATIP concern the generation of continuum states (in the potential of some bound-state electron density) as well as the computation of Auger and angular distribution parameters. By using this concept, we could incorporate for the first time interferences and the coherence transfer in the resonant excitation of $3d$ inner-shell electrons prior to a one- or two-step Auger cascade in atomic krypton [36]. Continuum spinors, however, are useful also for theoretical investigations on a number of other processes, including atomic photoexcitation and ionization, electron-impact ionization as well as the scattering of electrons. Therefore, the implementation of the RELCI component will prepare RATIP also for several more advanced applications.

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References

[1] J.P. Desclaux, Comput. Phys. Commun. 9 (1975) 31;
P. Indelicato, Private communication, 2000.
[2] I.P. Grant, B.J. McKenzie, P.H. Norrington, D.F. Mayers, N.C. Pyper, Comput. Phys. Commun. 21 (1980) 207; Comput. Phys. Commun. 21 (1980) 233.
[3] F.A. Parpia, C.F. Fischer, I.P. Grant, Comput. Phys. Commun. 94 (1996) 249.
[4] S. Fritzsche, C.F. Fischer, C.Z. Dong, Comput. Phys. Commun. 124 (2000) 342.
[5] S. Fritzsche, J. Elec. Spec. Rel. Phenom. 114–116 (2001) 1155.
[6] J.E. Sienkiewicz, S. Fritzsche, P. Syty, Acta Polon. 98 (2000) 41.
[7] F. von Busch, J. Doppelfeld, U. Kuetgens, S. Fritzsche, Phys. Rev. A 59 (1999) 2030.
[8] K. Ueda, Y. Shimizu, H. Chiba, M. Kitajimo, H. Tanaka, S. Fritzsche, N.M. Kabachnik, J. Phys. B 34 (2001) 107.
[9] Y. Shimizu, H. Yoshida, K. Okada, Y. Muramatsu, N. Saito, H. Ohashi, Y. Tamenori, S. Fritzsche, N.M. Kabachnik, H. Tanaka, K. Ueda, J. Phys. B 33 (2000) L685.
[10] Y.-K. Kirn, Private communication, 1999.
[11] G. Gaigalas, S. Fritzsche, I.P. Grant, Comput. Phys. Commun. 139 (2001) 263.
[12] I.P. Grant, J. Phys. B 7 (1974) 1458.
[13] I.P. Grant, in: S. Wilson (Ed.), Relativistic Effects in Atoms and Molecules, in: Methods in Computational Chemistry, Vol. 2, Plenum, New York, 1988, p. 1.
[14] G. Breit, Phys. Rev. 39 (1932) 616.
[15] G. Racah, Phys. Rev. 61 (1941) 186; Phys. Rev. 62 (1942) 438; Phys. Rev. 63 (1943) 367.
[16] J. Sapirstein, Phys. Scripta 36 (1987) 801.
[17] I.P. Grant, H.M. Quiney, in: D. Bates, B. Bederson (Eds.), in: Advances in Atomic and Molecular Physics, Vol. 23, Academic, New York, 1988, p. 37.
[18] W.R. Johnson, in: D. Liesen (Ed.), Physics with Multiply Charged Ions, in: NATO ASI Series, Vol. 348, Plenum Press, New York, London, 1995, p. 1.
[19] D.A. Varshalovich, A.N. Moskalev, V.K. Khersonskii, Quantum Theory of Angular Momentum, World Scientific, Singapore, 1988.

[20] I.P. Grant, N.C. Pyper, J. Phys. 9 (1976) 761.
[21] I.P. Grant, B.J. McKenzie, J. Phys. 13 (1980) 2671.
[22] E.A. Uehling, Phys. Rev. 48 (1935) 55.
[23] P.J. Mohr, Ann. Phys. (N.Y.) 88 (1974) 52; At. Data Nucl. Data Tables 29 (1983) 453.
[24] P.J. Mohr, Y.-K. Kirn, Phys. Rev. A 45 (1992) 2723.
[25] S. Fritzsche, C.F. Fischer, Comput. Phys. Commun. 99 (1997) 323.
[26] S. Fritzsche, I.P. Grant, Comput. Phys. Commun. 103 (1997) 277;
S. Fritzsche, J. Anton, Comput. Phys. Commun. 124 (2000) 354.
[27] G. Gaigalas, S. Fritzsche, Comput. Phys. Commun. 134 (2001) 86.
[28] E.R. Davidson, J. Comp. Phys. 17 (1975) 87.
[29] A. Stathopoulos, C.F. Fischer, Comput. Phys. Commun. 79 (1994) 268.
[30] G. Gaigalas, S. Fritzsche, Z. Rudzikas, At. Data Nucl. Data Tables 76 (2000) 235.
[31] C.Z. Dong, S. Fritzsche, B. Fricke, W.-D. Sepp, Monthly Notes Roy. Astron. Soc. 307 (1999) 809.
[32] A.K. Bhatia, G.A. Doschek, At. Data Nucl. Data Tables 66 (1995) 97.
[33] N.C. Deb, S.S. Tayal, At. Data Nucl. Data Tables 69 (1998) 161.
[34] S. Fritzsche, C.Z. Dong, E. Träbert, Monthly Notes Roy. Astron. Soc. 318 (2000) 263.
[35] J.R. Fuhr, W.C. Martin, A. Musgrove, J. Sugar, W.L. Wiese, NIST atomic spectroscopic database, URL http://physics.nist.gov/PhysRefData/contents.html, June 2000.
[36] M. Kitajima, M. Okamoto, Y. Shimizu, H. Chiba, S. Fritzsche, N.M. Kabachnik, I.P. Sazhina, F. Koike, T. Hayaishi, H. Tanaka, Y. Sato, K. Ueda, J. Phys. B 34 (2001) 3829.

TEST RUN OUTPUT

```
Storage initialization for the one- and two-partice effective
interaction strengths complete.
ANCO calculates the pair 1.0000000000000000E+06
ANCO calculates the pair 2.0000000000000000E+06
ANCO calculates the pair 3.0000000000000000E+06
ANCO calculates the pair 4.0000000000000000E+06
ANCO calculates the pair 5.0000000000000000E+06

Block J^P = (1/2,+): DVDSON routine selected for eigenvalue problem of
dimension 3375

RELCI Mixing Coefficient File generated.

Number of Dirac-Coulomb one-electron integrals computed = 21
Number of one-electron vacuum-polarization integrals computed = 21
Number of (full) one-electron matrix elements stored = 21
Number of (full) one-electron matrix elements re-used = 36970

Number of (full) two-electron X^k strengths computed = 5779
Number of (full) two-electron X^k strengths stored = 5715
Number of (full) two-electron X^k strengths re-used = 5715

Total number of Hamiltonian matrix elmenents refered to during
the diagonalization procedure = 3375

Average energy = -1.2195342030051697E+03

Eigenenergies:

Level J Parity Hartrees eV Kaysers

1 1/2 + -1.241300662872277D+03 -3.377752414074017D+04 -2.724340045467322D+08
2 1/2 + -1.240832140448524D+03 -3.376477499143883D+04 -2.723311757608137D+08
3 1/2 + -1.240696154749410D+03 -3.376107463070269D+04 -2.723013303497228D+08
4 1/2 + -1.240625232198285D+03 -3.375914472906454D+04 -2.722857646490079D+08
5 1/2 + -1.240100689843527D+03 -3.374487119922553D+04 -2.721706409094213D+08
6 1/2 + -1.239972929081823D+03 -3.374139465051999D+04 -2.721426006634309D+08
7 1/2 + -1.237857808846172D+03 -3.368383927577705D+04 -2.716783854308677D+08

Energy of each level relative to immediately lower level:

Level J Parity Hartrees eV Kaysers

2 1/2 + 4.685224237534840D-01 1.274914930134034D+01 1.028287859185944D+05
3 1/2 + 1.359856991143715D-01 3.700360736135153D+00 2.984541109088829D+04
4 1/2 + 7.092255112411294D-02 1.929901638152993D+00 1.556570071484811D+04
5 1/2 + 5.245423547585233D-01 1.427352983901513OD+01 1.151237395866444D+05
6 1/2 + 1.277607617039394D-01 3.476548705539681D+00 2.804024599036758D+04
7 1/2 + 2.115120235650920D+00 5.755537474293455D+01 4.642152325632803D+05

Energy of each level relative to lowest level:

Level J Parity Hartrees eV Kaysers
```

```
2 1/2 + 4.685224237534840D-01 1.274914930134034D+01 1.028287859185944D+05
3 1/2 + 6.045081228678555D-01 1.644951003747549D+01 1.326741970094827D+05
4 1/2 + 6.754306739919684D-01 1.837941167562849D+01 1.482398977243307D+05
5 1/2 + 1.199973028750492D+00 3.265294151464362D+01 2.633636373109752D+05
6 1/2 + 1.327733790454431D+00 3.612949022018330D+01 2.914038833013428D+05
7 1/2 + 3.442854026105351D+00 9.368486496311786D+01 7.556191158646231D+05

Weights of major contributors to ASF:

Level J Parity CSF contributions

1 1/2 + 0.71013 of 41 0.09779 of 7 0.06409 of 6 0.05723 of 2 0.03952 of 1
2 1/2 + 0.60113 of 5 0.18153 of 1 0.12347 of 2 0.03571 of 6 0.02467 of 7
3 1/2 + 0.43694 of 2 0.19821 of 1 0.19578 of 5 0.12343 of 6 0.00794 of 51
4 1/2 + 0.43729 of 1 0.26942 of 6 0.14408 of 2 0.07942 of 5 0.03179 of 7
5 1/2 + 0.25921 of 6 0.24270 of 41 0.20854 of 7 0.14098 of 2 0.08505 of 1
6 1/2 + 0.58542 of 7 0.20766 of 6 0.08666 of 5 0.05550 of 2 0.02076 of 1
7 1/2 + 0.32368 of 44 0.11678 of 65 0.06546 of 48 0.03782 of 49 0.03319
of 52

Entering QED ...

Orbital Self-energy estimate charge density ratio F(alphaZ)
(Hartree) this orbital / H-like

1s 0.1516E+00 0.962 0.2788112E+01
2s 0.1541E-01 0.712 0.3063832E+01
2p- -0.2979E-03 0.555 -0.7597774E-01
2p 0.5984E-03 0.552 0.1533623E+00
3s 0.2633E-02 0.403 0.3119283E+01
3p- -0.3349E-04 0.276 -0.5790357E-01
3p 0.9673E-04 0.275 0.1681534E+00
3d- -0.6478E-05 0.075 -0.4144610E-01
3d 0.0000E+00 0.070 0.0000000E+00
4s 0.5156E-02 1.861 0.3137555E+01
4p- -0.6486E-04 1.498 -0.4903624E-01
4p 0.2197E-03 1.427 0.1743839E+00
4d- -0.6374E-04 1.840 -0.3921667E-01
4d 0.0000E+00 1.401 0.0000000E+00
4f- 0.0000E+00 0.057 0.0000000E+00
4f 0.0000E+00 0.023 0.0000000E+00

... QED complete.

Self-energy corrections estimated --- these do not influence the data
in the RELCI mixing coefficients file.

Eigenenergies:

Level J Parity Hartrees eV Kaysers

1 1/2 + -1.240961286265239D+03 -3.376828922942503D+04 -2.723595199912410D+08
2 1/2 + -1.240490956830675D+03 -3.375549090883660D+04 -2.722562946122923D+08
3 1/2 + -1.240355027133936D+03 -3.375179207200328D+04 -2.722264614923019D+08
4 1/2 + -1.240284098427895D+03 -3.374986200288124D+04 -2.722108944407390D+08
5 1/2 + -1.239760188588505D+03 -3.373560568466854D+04 -2.720959095222294D+08
6 1/2 + -1.239631695674909D+03 -3.373210921308778D+04 -2.720677085874729D+08
```

```
7 1/2 + -1.237519047408079D+03 -3.367462110406783D+04 -2.716040358893536D+08

Energy of each level relative to immediately lower level:

Level J Parity Hartrees eV Kaysers

2 1/2 + 4.703294345632586D-01 1.279832058842280D+01 1.032253789487044D+05
3 1/2 + 1.359296967396438D-01 3.698836833328295D+00 2.983311999037772D+04
4 1/2 + 7.092870604108797D-02 1.930069122037378D+00 1.556705156297807D+04
5 1/2 + 5.239098393893716D-01 1.425631821270256D+01 1.149849185096005D+05
6 1/2 + 1.284929135962552D-01 3.496471580760067D+00 2.820093475653526D+04
7 1/2 + 2.112648266829829D+00 5.748810901994980D+01 4.636726981192188D+05

Energy of each level relative to lowest leve:

Level J Parity Hartrees eV Kaysers

2 1/2 + 4.703294345632586D-01 1.279832058842280D+01 1.032253789487044D+05
3 1/2 + 6.062591313029024D-01 1.649715742175110D+01 1.330584989390821D+05
4 1/2 + 6.771878373439904D-01 1.842722654378848D+01 1.486255505020602D+05
5 1/2 + 1.201097676733362D+00 3.268354475649104D+01 2.636104690116607D+05
6 1/2 + 1.329590590329617D+00 3.618001633725110D+01 2.918114037681959D+05
7 1/2 + 3.442238857159446D+00 9.366812535720089D+01 7.554841018874147D+05

RELCI complete ... .
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