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SOFTWARE FOR RELATIVISTIC ATOMIC THEORY : THE GRASP PROJECT AT OXFORD

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Résumé - GRASP est l'acronyme de General-purpose Relativistic Atomic Structure Program. Ce progiciel est essentiellement un code Dirac-Fock multiconfigurationnel (MCDF) convivial basé sur l'algèbre de Racah et les méthodes de différences finies. Nous décrivons ici brièvement le formalisme MCDF dans le contexte du projet GRASP à Oxford.

Abstract - GRASP is an acronym for General-purpose Relativistic Atomic Structure Program. This package is essentially a user-friendly multiconfiguration Dirac-Fock (MCDF) code based on the Racah Algebra and finite-difference methods. We describe briefly the MCDF formalism in the context of the GRASP project at Oxford.

1 - Introduction

Relativistic atomic theory is known to provide an economical and reliable approach to the estimation of the static and dynamic properties of highly-charged ions. There are, however, numerous other niches in atomic theory where the relativistic formalism is a felicitous choice: for instance, inner-shell processes in heavy atoms, the calculation of term energies to spectroscopic accuracy, and, quite generally, any situation in which strong configuration mixing is evident.

The needs of physicists investigating processes that occupy the niches best studied with relativistic atomic theory have been addressed to some extent by three software projects at Oxford University. In the following sections of this article we treat only the GRASP structure package. The two other codes, JJMTRX ⁽¹⁾ — a relativistic R-matrix

⁽¹⁾ The JJMTRX project is a collaboration between The Queen's University of Belfast and Oxford University.

suite for electron-atom/ion collision and photoionization calculations — and SWIRLES ⁽²⁾ — a basis-set Dirac-Fock/relativistic many-body perturbation theory structure program — will be described elsewhere.

We adopt a naïve approach to relativistic atomic structure theory. (Readers wishing to begin from a more rigorous foundation should consult the literature — cf. /1/, for instance.) In section 2, we thus build N -electron Hamiltonians from one- and two-particle component Hamiltonians. The construction of wavefunctions for N -electron atoms from one-electron orbitals is described in broad outline in section 3. A similar method is adopted for the exposition of the multiconfiguration Dirac-Fock (MCDF) method in section 4. The theory is motivated with concrete examples.

2 - Relativistic Hamiltonians

A Hamiltonian, $\hat{H}$, for the $i = 1, \dots, N$ electrons of an atomic system is a sum of N one-body contributions, $\hat{H}^{(1)}(i)$ and $N(N-1)/2$ two-body contributions, $\hat{H}^{(2)}(ij)$,

$$\hat{H} = \sum_{i=1}^N \hat{H}^{(1)}(i) + \sum_{\substack{i,j=1 \\ i \neq j}}^N \hat{H}^{(2)}(ij). \quad (2-1)$$

Symbols representing operators are distinguished by placing carets over them.

The dominant relativistic corrections to atomic structure are ultimately due to modifications to the one-body terms in the Hamiltonian. Current usage therefore classifies the formalism as relativistic when the one-body operators, $\hat{H}^{(1)}(i)$, are based upon the Dirac kinetic energy operator, $\hat{H}^D(i)/2$,

$$\hat{H}^D(i) = c \vec{\alpha}(i) \cdot \vec{p}(i) + \left(\tilde{\beta}(i) - \tilde{1}(i) \right) c^2. \quad (2-2)$$

Symbols representing matrices are distinguished by placing tildes over them. Here and elsewhere we make use of Hartree atomic units: $e = h/2\pi = m_e = 1$, whence $c = 1/\alpha$; e is the charge on the proton, h is Planck's constant, m_e is the rest mass of the electron, c is the speed of light in the vacuum and $\alpha \approx 1/137$ is the fine-structure constant. In Eq. (2-2), $\vec{\alpha}(i) \cdot \vec{p}(i) = \tilde{\alpha}_x(i) \hat{p}_x(i) + \tilde{\alpha}_y(i) \hat{p}_y(i) + \tilde{\alpha}_z(i) \hat{p}_z(i)$; the $\tilde{\alpha}$'s here and the $\tilde{\beta}$ in Eq. (2-2) are Dirac matrices (cf., for instance, /3/); the $\hat{p}$'s are the Cartesian components of the momentum operator. When the nucleus is modelled as a spherically-symmetric distribution of charge, the relativistic one-body operator takes the form

$$\hat{H}^{(1)}(i) = \hat{H}^D(i) + V_{\text{nuc}}(\hat{r}(i)). \quad (2-3)$$

The simplest two-body operator we consider is that arising from the Coulomb interaction,

$$\hat{H}^C(ij) = \hat{R}^{-1}(ij) \quad (2-4)$$

where $\vec{R}(ij) = \vec{r}(i) - \vec{r}(j)$. The resulting Hamiltonian, known as the Dirac-Coulomb Hamiltonian, is denoted $\hat{H}^{\text{DC}}$.

⁽²⁾ The SWIRLES project is a collaboration between Oxford University and the Rutherford Appleton Laboratory.

Quantum electrodynamics (QED) (cf., for instance, /3/) predicts additional two-body interactions. The dominant correction to the Coulomb interaction, due to the exchange of a single transverse photon of energy ω between a pair of electrons i and j , contributes

$$\begin{aligned} \hat{H}^{\text{trans}}(ij) = & -\vec{\alpha}(i) \cdot \vec{\alpha}(j) \left(\frac{\cos(\omega \hat{R}(ij))}{\hat{R}(ij)} \right) \\ & - \left(\vec{\alpha}(i) \cdot \vec{\nabla}(i) \right) \left(\vec{\alpha}(j) \cdot \vec{\nabla}(j) \right) \left(\frac{\cos(\omega \hat{R}(ij)) - 1}{\omega^2 \hat{R}(ij)} \right) \end{aligned} \quad (2-5)$$

to the energy. The $\omega \rightarrow 0$ limit of $\hat{H}^{\text{trans}}$, known as the Breit interaction /4/,

$$\hat{H}^{\text{Breit}}(ij) = -\frac{\vec{\alpha}(i) \cdot \vec{\alpha}(j)}{2\hat{R}(ij)} - \frac{(\vec{\alpha}(i) \cdot \vec{\hat{R}}(ij))(\vec{\alpha}(j) \cdot \vec{\hat{R}}(ij))}{2\hat{R}^3(ij)}, \quad (2-6)$$

accounts for the dominant part of the transverse interaction. The Breit interaction is the sum of the Gaunt (or magnetic) interaction /5/, $\hat{H}^{\text{Gaunt}}(ij) = -\vec{\alpha}(i) \cdot \vec{\alpha}(j)/\hat{R}(ij)$, and the lowest-order retardation correction to the electrostatic interaction /4/, $\hat{H}^{\text{ret}}(ij) = \vec{\alpha}_i \cdot \vec{\alpha}_j/2\hat{R}(ij) - [\vec{\alpha}(i) \cdot \vec{\hat{R}}(ij)][\vec{\alpha}(j) \cdot \vec{\hat{R}}(ij)]/2\hat{R}^3(ij)$.

Nuclear motion also introduces contributions to the energy. The major effect is a rescaling of the energy of the form

$$E_{\Gamma} \rightarrow \mu E_{\Gamma} \quad (2-7)$$

where E_{Γ} is an atomic energy level and $\mu = A/(1 + A)$ where $A = M_{\text{nuc}}/m_e$ and M_{nuc} is the mass of the nucleus.

The theory outlined so far may be inadequate for certain high-precision calculations: the correlated motions of the electrons introduce additional corrections to the nuclear motional energy; the detailed structure of the nucleus has been neglected entirely; we have not considered the influence of the virtual electron-positron pairs which arise from the fluctuation of the vacuum — principally the self-energy and vacuum-polarization corrections. These effects are, however, of higher order than those discussed above and are consistently treated by a perturbation-theory approach to QED (cf., for instance, /1/).

3 - Relativistic Wavefunctions

Atomic calculations are usually based upon the orbital approximation. In relativistic atomic physics, an orbital, $|nljm\rangle$, is a simultaneous eigenfunction of the parity operator, $\hat{\pi}$, and the angular momentum operator, $\vec{j} = \vec{l} + \vec{s}$; thus,

$$\begin{aligned} \hat{\pi} |nljm\rangle &= (-1)^l |nljm\rangle, \\ \hat{j}^2 |nljm\rangle &= j(j+1) |nljm\rangle, \\ \hat{j}_z |nljm\rangle &= m |nljm\rangle, \quad m = -j, \dots, j, \end{aligned} \quad (3-1)$$

Here n is the principal quantum number. We require that the orbitals form an orthonormal set,

$$\langle n_a l_a j_a m_a | n_b l_b j_b m_b \rangle = \delta_{ab}. \quad (3-2)$$

The quantum numbers l, j and m provide a complete specification of the symmetry. Each of the $\leq (2j+1)$ orbitals with the same j but differing m quantum numbers, referred to as a subshell, are assumed to have the same radial form. Using the conventions of /6/, an explicit representation is thus

$$\langle \vec{r} | n l j m \rangle = \frac{1}{r} \begin{pmatrix} P_{nlj}(r) \chi_{ljm}(\vec{r}/r) \\ i Q_{nlj}(r) \bar{\chi}_{ljm}(\vec{r}/r) \end{pmatrix}. \quad (3-3)$$

Here $P_{nlj}(r)$ and $Q_{nlj}(r)$ are, respectively, the large and small component radial wavefunctions, and the functions $\chi_{ljm}(\vec{r}/r)$ are the spinor spherical harmonics,

$$\chi_{ljm}(\vec{r}/r) = \sum_{\sigma=\pm\frac{1}{2}} \langle l m - \sigma \frac{1}{2} \sigma | l \frac{1}{2} j m \rangle Y_l^{m-\sigma}(\vec{r}/r) \phi^\sigma, \quad (3-4)$$

where $\langle l m - \sigma \frac{1}{2} \sigma | l \frac{1}{2} j m \rangle$ is a Clebsch-Gordan coefficient, $Y_l^{m-\sigma}(\vec{r}/r)$ is a spherical harmonic and ϕ^σ is a spinor basis function. For a given value of j the quantum number l can take the values $l = j \pm \frac{1}{2}$. The appropriate barred spinor, $\bar{\chi}_{ljm}$, in Eq. (3-3) is then obtained by choosing $l = j \mp \frac{1}{2}$ in Eq. (3-4).

A configuration state function (CSF), $|\gamma J^P M\rangle$, of an N -electron system is formed by linearly combining Slater determinants of order N constructed from the orbitals (3-3) so as to obtain eigenfunctions of the parity operator, $\hat{\Pi} = \hat{\pi}_1 \cdots \hat{\pi}_N$, and total angular momentum operator, $\vec{J} = \vec{J}_1 + \cdots + \vec{J}_N$; thus

$$\begin{aligned} \hat{\Pi} |\gamma J^P M\rangle &= P |\gamma J^P M\rangle, \quad P = (-1)^{l_1 + \cdots + l_N}, \\ \hat{J}^2 |\gamma J^P M\rangle &= J(J+1) |\gamma J^P M\rangle, \\ \hat{J}_z |\gamma J^P M\rangle &= M |\gamma J^P M\rangle, \quad M = -J, \dots, J. \end{aligned} \quad (3-5)$$

Any additional information required to uniquely specify the construction of the CSF is represented by the symbol γ . We require orthonormality of the CSFs, $\langle \gamma_r J_r^P M_r | \gamma_s J_s^P M_s \rangle = \delta_{rs}$.

An (approximate) atomic state function (ASF), $|\Gamma J^P M\rangle$, is a linear combination of CSFs with the given eigenvalues J, P , and M . Because the transformation matrix elements, $c_{r\Gamma} = \langle \gamma_r J^P M | \Gamma J^P M \rangle$, are independent of the quantum number M , the entire set of $(2J+1)$ transformation equations may be written

$$|\Gamma J^P\rangle = \sum_{r=1}^{n_{JP}} c_{r\Gamma} |\gamma_r J^P\rangle; \quad (3-6)$$

n_{JP} is then the number of levels with quantum numbers J and P . The mixing coefficients, $c_{r\Gamma}$, may be combined in a column vector, $\tilde{c}_\Gamma \equiv \{c_{r\Gamma}, r = 1, \dots, n_{JP}\}$, the representation of the ASF $|\Gamma J^P M\rangle$ with respect to the CSFs $|\gamma_r J^P M\rangle, r = 1, \dots, n_{JP}$. This procedure effectively partitions the space of CSFs into subspaces characterised by states sharing the eigenvalues J, P and M . The ASFs will be chosen to be orthonormal, so that

$$(\tilde{c}_{\Gamma_i})^\dagger \tilde{c}_{\Gamma_j} = \delta_{ij}; \quad (3-7)$$

the dagger denotes the Hermitian conjugate.

4 - GRASP

Approximate eigenenergies (or first-order perturbative corrections to approximate eigenenergies) of free atoms are then obtained as diagonal expectation values of the approximate Hamiltonians (or perturbation Hamiltonians) with respect to ASFs. For instance,

$$E_F^{\text{DC}} \equiv \langle \Gamma J^P M | \hat{H}^{\text{DC}} | \Gamma J^P M \rangle. \quad (4-1)$$

These energies are independent of the eigenvalue M by construction, and are therefore $(2J + 1)$ -fold degenerate.

The Dirac-Coulomb Hamiltonian matrix, $\tilde{H}^{\text{DC}}$, with elements

$$H_{rs}^{\text{DC}} = \langle \gamma_r J_r^{P_r} M_r | \hat{H}^{\text{DC}} | \gamma_s J_s^{P_s} M_s \rangle \delta_{J_r J_s} \delta_{P_r P_s} \delta_{M_r M_s}, \quad (4-2)$$

plays a central role in the GRASP implementation of the multiconfiguration Dirac-Fock (MCDF) theory. The matrix elements H_{rs}^{DC} are also independent of M with a degeneracy of $(2J + 1)$. They may be written as sums of products of angular coefficients and radial integrals,

$$H_{rs}^{\text{DC}} = \sum_{i=1}^{N_{rs}^{(T)}} T_{rs}(a_i b_i) I(a_i b_i) + \sum_{i=1}^{N_{rs}^{(V)}} V_{rs}^{(k_i)}(a_i b_i c_i d_i) R^{(k_i)}(a_i b_i c_i d_i). \quad (4-3)$$

The one-body contributions (2-3) give rise to the $T_{rs}(ab)$ angular coefficients and the $I(ab)$ radial integrals,

$$\begin{aligned} I(ab) = & \delta_{l_a l_b} \delta_{j_a j_b} \int_0^\infty dr \left[c (Q_{n_a l_a j_a}(r) P'_{n_b l_b j_b}(r) - P_{n_a l_a j_a}(r) Q'_{n_b l_b j_b}(r)) \right. \\ & - 2c^2 Q_{n_a l_a j_a}(r) Q_{n_b l_b j_b}(r) \\ & + \frac{c\kappa_a}{r} (P_{n_a l_a j_a}(r) Q_{n_b l_b j_b}(r) + Q_{n_a l_a j_a}(r) P_{n_b l_b j_b}(r)) \\ & \left. + V_{\text{nuc}}(r) (P_{n_a l_a j_a}(r) P_{n_b l_b j_b}(r) + Q_{n_a l_a j_a}(r) Q_{n_b l_b j_b}(r)) \right], \end{aligned} \quad (4-4)$$

where $f' \equiv df/dr$ and $\kappa = -(2j + 1)(j - l)$; the interelectronic interactions (2-4) yield the $V_{rs}^{(k)}(abcd)$ angular coefficients and the relativistic Slater integrals, $R^{(k)}(abcd)$,

$$R^{(k)}(abcd) = \int_0^\infty dr \left[(P_{n_a l_a j_a}(r) P_{n_c l_c j_c}(r) + Q_{n_a l_a j_a}(r) Q_{n_c l_c j_c}(r)) \frac{1}{r} Y^{(k)}(bd; r) \right]; \quad (4-5)$$

the relativistic Hartree Y -functions are defined by the equation

$$Y^{(k)}(ab; r) = r \int_0^\infty ds \frac{r_{<}^k}{r_{>^{k+1}}} (P_{n_a l_a j_a}(s) P_{n_b l_b j_b}(s) + Q_{n_a l_a j_a}(s) Q_{n_b l_b j_b}(s)). \quad (4-6)$$

Here $r_{>} (r_{<})$ denotes the greater (lesser) of r and s .

A prerequisite for the development of a Racah-algebra based program to compute the angular coefficients $T_{rs}(ab)$ and $V_{rs}^{(k)}(abcd)$ is a code to determine jj -coupled coefficients of fractional parentage. Such a program, CFPJJ /7/, was made available through the *Computer Physics Communications Program Library* in 1972.

A second package, MCP /8/, to compute the $V_{rs}^{(k)}(abcd)$ coefficients, followed shortly thereafter, in 1973. This code was revised and reissued as MCP75 /9/ in 1976. Either MCP package accepts a list of CSF specifications $(\gamma_r J_r^{P_r})$ (specifying the value of M is unnecessary — cf. Eq. (4-2)) and computes the value, $V_{rs}^{(k_i)}(a_i b_i c_i d_i)$, and all indices, k_i , a_i , b_i , c_i , d_i , of each coefficient for each pair γ_r and γ_s that interact: i.e., have nonzero matrix elements H_{rs} . The total number of coefficients for such a pair is denoted $N_{rs}^{(V)}$ (cf. Eq. (4-3)). (The MCP package used in the recent versions of the Oxford MCDF packages are modified to compute only those coefficients that cannot be expressed in very simple analytical forms.) The user-friendly input interface as implemented in the module CSFIN in MCP is the precursor of the current GRASP interface routine CARDIN.

A major rewrite /10/ of the RDMEJJ package of Chang /11/, now called MCT, was released in 1978. This code computes angular coefficients, $T_{rs}^{(k\pi)}(ab)$, required to calculate matrix elements of a general one-particle tensor operator of rank k and parity π ,

$$\hat{F}^{(k\pi)} = \sum_{i=1}^N \hat{f}_q^{(k\pi)}(i) \quad (4-7)$$

in a CSF basis,

$$\begin{aligned} \langle \gamma_r J_r^{P_r} M_r | \hat{F}^{(k\pi)} | \gamma_s J_s^{P_s} M_s \rangle &= (-1)^{J_r - M_r} \begin{pmatrix} J_r & k & J_s \\ M_r & q & -M_s \end{pmatrix} \\ &\times \sum_{i=1}^{N_{rs}^{(T(k\pi))}} T_{rs}^{(k\pi)}(a_i b_i) (n_{a_i} l_{a_i} j_{a_i} | \hat{f}^{(k\pi)}(r) | n_{b_i} l_{b_i} j_{b_i}). \end{aligned} \quad (4-8)$$

The coefficients $T_{rs}(ab)$ in Eq. (4-3) are those appropriate to scalar operators ($k = 0$, $\pi = +1$).

The requisite triad of angular packages for MCDF computations was completed in 1980 with a generalization (published as part of MCBP/BENA /12/) of the original MCBP package /13/ to finite photon frequencies. The present version of MCBP computes the angular coefficients $V_{rs}^{(k\tau)}(abcd)$ for the evaluation of the matrix elements of the transverse interaction (2-5),

$$\begin{aligned} H_{rs}^{\text{transv}} &= \langle \gamma_r J_r^{P_r} M_r | \hat{H}^{\text{transv}} | \gamma_s J_s^{P_s} M_s \rangle \delta_{J_r J_s} \delta_{P_r P_s} \delta_{M_r M_s} \\ &= \sum_{i=1}^{N_{rs}^{\text{transv}}} V_{rs}^{(k_i \tau_i)}(a_i b_i c_i d_i) S_{rs}^{(k_i \tau_i)}(a_i b_i c_i d_i) \end{aligned} \quad (4-9)$$

The $S_{rs}^{(k_i \tau_i)}(a_i b_i c_i d_i)$ are radial integrals /14/ that are appreciably more complex than the Slater integrals given by Eq. (4-5).

With the appropriate generalization of a Dirac-Fock (DF⁽³⁾) self-consistent field (SCF) code due to D.F. Mayers, it was possible to construct the MCDF+MCBP/BENA /15,12/ pair of packages, which were published in 1980.

⁽³⁾ The Dirac-Fock model is obtained when a single Slater determinant can be used to model the atomic state.

GRASP /16/, published in 1989, is a major rewrite of the MCDF+MCBP/BENA /15,12/ package. The portability and currency of the program have been greatly enhanced by recoding from FORTRAN IV to approach the FORTRAN 77 standard. A preprocessor forms an important part of the package: the source code is issued in raw form which must be preprocessed to FORTRAN source code — the preprocessor performs basic editing operations using data from a user-created symbol file to select machine- and installation-dependent code and to set array dimensions; the problem to be solved is thus limited only by the stability of the SCF solver and the available storage. Both the (rewritten) MCDF /15/ and MCBP/BENA /12/ modules as well as the TRANSFORM /17/ and OSLC packages have been integrated into the stand-alone GRASP code; using the facilities available in TRANSFORM /17/ the user can perform recoupling from the standard jj -coupling of GRASP to nonstandard jj -, LS - or jl -coupled eigenvector bases; the OSLC package computes radiative transition data with retardation to all orders. The increased capability has necessitated modifications to the interface which has also been rendered more flexible and easy to use. Much effort has been expended to improve efficiency: the Jucys-graph based NJGRAF /18/ package replaces the algebra-based NJSYM /19/ for the computation of angular recoupling coefficients; the SCF algorithm is faster and more stable; the $V_{rs}^{(k)}(abcd)$ and $T_{rs}^{(k\pi)}(ab)$ coefficients are sorted into an integral-based, rather than a CSF-based list — for instance, it is more efficient to compute the radial integrals in (4-3) only once and then accumulate their contributions to each matrix element H_{rs}^{DC} rather than to compute all required integrals each time a matrix element is to be computed; radial integrals can be stored — this obviates the need to recompute a part of them if some of the orbitals remain unchanged between calculations. Variations on the MCDF method — the freezing of certain orbitals and the Slater exchange approximation, for instance — are available. By the use of the integral scaling facility, GRASP eigenvalues may be made to match experimental data. The accuracy and reliability of the results have been improved — all errors known prior to publishing have been eliminated and more accurate numerical methods are used. The program is internally documented to some extent with plentiful comment cards. A User's Manual provides help in the set-up and use of the package, complete specification of the input and some information about the program's structure and operation.

GRASP² (PARPIA, F.A., GRANT, I.P., DYALL, K.G., and FISCHER, C.F., in preparation) is a major rewrite of GRASP. It is based on a completely new SCF algorithm adapted from procedures developed and extensively used by Fischer (cf., for instance, /20/) for the nonrelativistic multiconfiguration Hartree-Fock method. Testing has revealed that great gains have been made, both in stability and in efficiency, when GRASP² is compared with its predecessors. Full FORTRAN 77 compatibility has been attained. Some minor errors carried over from GRASP have been eliminated. The relativistic local-density approximation for exchange and correlation effects (cf. /21/, for instance) is available as an option. The User's Manual that accompanies the program is now a complete reference document: besides a set of tutorials on the set-up and use of the package and a detailed description of the input Command/Data File structure, the underlying physical and numerical formalism, the flow structure and each subroutine of the code are explained. The GRASP² package is in the final stages of testing and should be available before the end of 1990.

GRASP³, now in the early stages of development, will extend the capabilities of GRASP² to the calculation of dynamic phenomena (photoionization, electron-atom/ion

scattering, etc.) involving a single continuum electron. We expect that this program will be released by the end of 1992.

We motivate the principal classes of MCDF procedures as implemented in GRASP² with two examples. Consider the estimation of the energies of the seven lowest-lying levels of heliumlike Argon, Ar^{16+} ,

$$\begin{aligned}
 |(00000000.00 \text{ cm}^{-1}) 1 0^+ &\xrightarrow{c \rightarrow \infty} |1s^2 1S_0^e\rangle, \\
 |(25036594.11 \text{ cm}^{-1}) 2 1^+ &\xrightarrow{c \rightarrow \infty} |1s2s 3S_1^e\rangle, \\
 |(25187779.82 \text{ cm}^{-1}) 2 0^- &\xrightarrow{c \rightarrow \infty} |1s2p 3P_0^o\rangle, \\
 |(25192958.84 \text{ cm}^{-1}) 2 1^- &\xrightarrow{c \rightarrow \infty} |1s2p 3P_1^o\rangle, \\
 |(25200959.64 \text{ cm}^{-1}) 2 0^+ &\xrightarrow{c \rightarrow \infty} |1s2s 1S_0^e\rangle, \\
 |(25215171.18 \text{ cm}^{-1}) 2 2^- &\xrightarrow{c \rightarrow \infty} |1s2p 3P_2^o\rangle, \\
 |(25322387.43 \text{ cm}^{-1}) 2 1^- &\xrightarrow{c \rightarrow \infty} |1s2p 1P_1^o\rangle,
 \end{aligned} \tag{4-10}$$

where the excitation energy with respect to the ground state (computed from the ionization energies in cm^{-1} as given by Drake /22/) appears in parentheses on the left-hand side, and the designation of the state in the nonrelativistic limit is given on the right-hand side, of each line. For this problem, it is well known that the most important CSFs are, respectively,

$$\begin{aligned}
 |1 0^+ &\approx |1s_{1/2}^2 0^+\rangle, \\
 |2 1^+ &\approx |1s_{1/2} 2s_{1/2} 1^+\rangle, \\
 |2 0^- &\approx |1s_{1/2} 2p_{1/2} 0^-\rangle, \\
 |2 1^- &\approx a|1s_{1/2} 2p_{1/2} 1^-\rangle + b|1s_{1/2} 2p_{3/2} 1^-\rangle, \\
 |2 0^+ &\approx |1s_{1/2} 2s_{1/2} 0^+\rangle, \\
 |2 2^- &\approx |1s_{1/2} 2p_{3/2} 2^-\rangle, \\
 |2 1^- &\approx c|1s_{1/2} 2p_{3/2} 1^-\rangle + d|1s_{1/2} 2p_{1/2} 1^-\rangle.
 \end{aligned} \tag{4-11}$$

(The quantum number M has been suppressed on both sides of each approximate equality.) An array of $7^2 = 49$ elements is needed to store all unique values of H_{rs}^{DC} ,

$$\tilde{H}^{\text{DC}} = \begin{pmatrix} H_{11}^{\text{DC}} & 0 & 0 & 0 & H_{15}^{\text{DC}} & 0 & 0 \\ 0 & H_{22}^{\text{DC}} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & H_{33}^{\text{DC}} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & H_{44}^{\text{DC}} & 0 & 0 & H_{47}^{\text{DC}} \\ H_{51}^{\text{DC}} & 0 & 0 & 0 & H_{55}^{\text{DC}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & H_{66}^{\text{DC}} & 0 \\ 0 & 0 & 0 & H_{74}^{\text{DC}} & 0 & 0 & H_{77}^{\text{DC}} \end{pmatrix}, \tag{4-12}$$

where the order of the CSFs is as they appear in the first term on the right in each line of Eq. (4-11). This matrix is actually symmetric (by virtue of the phase convention adopted in the GRASP project; the matrix would be Hermitian otherwise — cf. Eq. (4-4)). It is therefore necessary to compute only 28 of the 49 elements. Those set to zero must take this value because of the selection rules on parity and angular momentum (explicitly shown in Eq. (4-2)).

TIME 100	Guess that 100 s of CPU time is required — this strongly depends on the computer employed.
He-like Ar	This string is written as an identifier in all GRASP ² files (including the print output). The title card also delimits the beginning of a case.
7 4	The basic dimensions of the case: $r = 1, \dots, n_c = 7$ and $a = 1, \dots, n_w = 4$.
1S 2 1 1 1 1 1	Each column here gives the occupation $q_r(a)$ of electrons in the four subshells $n_a l_a j_a$ in a given $\gamma_r J_r^{P_r}$; 2P- represents the $2p_{1/2}$ subshell, 2P, the $2p_{3/2}$ subshell.
2S 0 1 0 0 1 0 0	
2P- 0 0 1 1 0 0 0	
2P 0 0 0 0 0 1 1	
ANG	Any additional information required to complete the specification of the $\gamma_r J_r^{P_r}$ follows this card.
2 1	Very little additional information is required for the two-electron problem — none if the subshell is full, as it is for $r = 1$, and only the total angular momentum J_r obtained by coupling the angular momenta j_a otherwise. The first number in each row is r , the second is J_r .
3 0	
4 1	
5 0	
6 2	
7 1	
MCP 7 8	Compute the $V_{rs}^{(k)}(abcd)$ and $T_{rs}(ab)$ coefficients; write the CSF-based list on unit 7, the integral-based list on unit 8.
MCDF 25	Generate the radial functions using the AL approximation; read the integral-based list of $V_{rs}^{(k)}(abcd)$ and $T_{rs}(ab)$ coefficients on unit 8; there is no MCDF Dump File from which the SCF procedure can be restarted — hence the 0; write the MCDF Dump File on unit 9; the atomic number of Argon is 18; the atomic weight, 39.948 amu, is used internally to estimate both the nuclear radius and the reduced mass of the electron.
8 0 9	
18 39.948	
AL	
MCBP 12	Compute the $V_{rs}^{(k\tau)}(abcd)$ coefficients and write them out on unit 12. No sorting is done.
BENA	Compute the higher-order corrections: diagonalise $\hat{H}^{\text{trans}}$ and estimate the self-energy and vacuum-polarization contributions.
8 9 12	Read the integral-based list of $V_{rs}^{(k)}(abcd)$ and $T_{rs}(ab)$ coefficients on unit 8, the MCDF Dump File on unit 9 and the $V_{rs}^{(k\tau)}(abcd)$ coefficients on unit 12.
MCT 11 12 0 -1	Compute the $T_{rs}^{(k\pi)}(ab)$ coefficients for $k = 1$, and odd parity; write the CSF-based list on unit 11 and the integral-based list on unit 12; there is no restart file from which any CSF-based list can be read: hence the 0.
OSCL	Compute electromagnetic transition data: oscillator strengths, Einstein A and B coefficients, etc.
9 12	Read the MCDF Dump File on unit 9 and the $T_{rs}^{(k\pi)}(abcd)$ coefficients on unit 12.
END	This card delimits the end of a case.

Figure 1. A typical GRASP² Command/Data File. Each card is briefly explained with the comments that appear to the right of it. A detailed description of the overall structure and the structure of each individual card of the Command/Data File may be found in the User's Manual that is issued with the program.

We make use of the member with $M = 0$ in Eq. (4-1) — this value of M is universal to all states in systems with an even number of electrons (we would similarly use $M = \pm \frac{1}{2}$ for cases with an odd number of electrons). The energies of all seven atomic levels are then given by equations of the form (cf. Eq. (4-11))

$$E_{\Gamma}^{\text{DC}} = \langle \Gamma J^P 0 | \hat{H}^{\text{DC}} | \Gamma J^P 0 \rangle = (\tilde{c}_{\Gamma}^{\text{DC}})^{\dagger} \tilde{H}^{\text{DC}} \tilde{c}_{\Gamma}^{\text{DC}}. \quad (4-13)$$

The optimal values of the mixing coefficient vectors, $\tilde{c}$ are obtained by requiring E_{Γ}^{DC} to be stationary with respect to variations in the mixing coefficients subject to Eq. (3-7). This leads to an eigenvalue problem,

$$(\tilde{H}^{\text{DC}} - E_{\Gamma}^{\text{DC}} \tilde{I}) \tilde{c}_{\Gamma}^{\text{DC}} = 0. \quad (4-14)$$

Here $\tilde{I}$ is the $n_c \times n_c$ unit matrix, where $n_c = \sum_{JP} n_{JP}$ and we have appropriately extended the mixing coefficient vectors with elements 0 for components in orthogonal subspaces.

The eigenvalue problem given by Eq. (4-14) above can be solved once the matrix $\tilde{H}^{\text{DC}}$ has been constructed. We have seen that this requires knowledge of the angular coefficients $V_{rs}^{(k)}(abcd)$ and $T_{rs}(ab)$ and the orbital radial functions $P_{nlj}(r)$, $Q_{nlj}(r)$, so that the diagonalization (4-14) is the last step, and the determination of the Hamiltonian matrix (4-12) the penultimate one, in any computational procedure based on the formalism outlined so far.

The first computational step is performed by MCP (which in turn calls the relevant subroutines in MCT) to determine the angular coefficients $V_{rs}^{(k)}(abcd)$ and $T_{rs}(ab)$; these coefficients are written to a disk file: it is economical to break up an atomic structure problem into its radial and angular parts — one can thus avoid recomputing the angular coefficients for calculations along an isoelectronic sequence, for instance.

The problem of the selection of the functions $P_{nlj}(r)$, $Q_{nlj}(r)$ now arises. These are determined as the numerical solutions of coupled pairs of radial Dirac equations of the form

$$\begin{aligned} \left(\frac{d}{dr} + \frac{\kappa_a}{r} \right) P_{n_a l_a j_a}(r) - \left(2c - \frac{\epsilon_{aa}}{c} + \frac{\mathcal{Y}_a(r)}{cr} \right) Q_{n_a l_a j_a}(r) &= -\frac{\mathcal{X}_a^{(P)}(r)}{r}, \\ \left(\frac{d}{dr} - \frac{\kappa_a}{r} \right) Q_{n_a l_a j_a}(r) + \left(-\frac{\epsilon_{aa}}{c} + \frac{\mathcal{Y}_a(r)}{cr} \right) P_{n_a l_a j_a}(r) &= -\frac{\mathcal{X}_a^{(Q)}(r)}{r}, \end{aligned} \quad (4-15)$$

with $\epsilon_{aa} > 0$ subject to the boundary conditions

$$P_{n_a l_a j_a}(r), Q_{n_a l_a j_a}(r) \xrightarrow{r \rightarrow 0} 0, \quad P_{n_a l_a j_a}(r), Q_{n_a l_a j_a}(r) \xrightarrow{r \rightarrow \infty} 0, \quad (4-16)$$

the orthonormalization condition which follows from Eq. (3-2),

$$\begin{aligned} \mathcal{N}(ab) &= \begin{cases} 0 & \text{when } a \neq b \text{ but } l_a = l_b \text{ and } j_a = j_b, \\ 1 & \text{when } a = b, \end{cases} \\ \mathcal{N}(ab) &\equiv \int_0^\infty dr (P_{n_a l_a j_a}(r) P_{n_b l_b j_b}(r) + Q_{n_a l_a j_a}(r) Q_{n_b l_b j_b}(r)), \end{aligned} \quad (4-17)$$

and that the sign of the first oscillation of $P_{n_a l_a j_a}(r)$ that exceeds a certain amplitude be positive and that the total number of such oscillations be $n_a - l_a - 1$ (cf. /20/, for instance).

The asymptotic forms of, and the relation between, the large- and small-component functions near the origin are dependent upon the detailed behaviour of the functions $\mathcal{Y}_a(r)$, $\mathcal{X}_a^{(P)}(r)$ and $\mathcal{X}_a^{(Q)}(r)$ in this neighbourhood.

The latter functions are given by the expressions

$$\begin{aligned}
 \mathcal{Y}_a(r) &= -rV_{\text{nuc}}(r) - \sum_{i=1}^{N_a^{(y)}} y_a^{(k_i)}(b_i c_i) Y^{(k_i)}(b_i c_i; r), \\
 \mathcal{X}_a^{(P)}(r) &= \frac{1}{c} \sum_{i=1}^{N_a^{(x)}} x_a^{(k_i)}(b_i c_i d_i) Y^{(k_i)}(b_i c_i; r) Q_{n_{d_i} l_{d_i} j_{d_i}}(r) + \frac{r}{c\bar{q}(a)} \sum_{i=1}^{N_a^{(\epsilon)}} \epsilon_{ab_i} Q_{n_{b_i} l_{b_i} j_{b_i}}(r) \\
 &\quad + r \sum_{i=1}^{N_a^{(z)}} z_a(b_i) \left[\left(\frac{d}{dr} + \frac{\kappa_{b_i}}{r} \right) P_{n_{b_i} l_{b_i} j_{b_i}}(r) - \left(2c - \frac{V_{\text{nuc}}(r)}{c} \right) Q_{n_{b_i} l_{b_i} j_{b_i}}(r) \right], \\
 \mathcal{X}_a^{(Q)}(r) &= -\frac{1}{c} \sum_{i=1}^{N_a^{(x)}} x_a^{(k_i)}(b_i c_i d_i) Y^{(k_i)}(b_i c_i; r) P_{n_{d_i} l_{d_i} j_{d_i}}(r) - \frac{r}{c\bar{q}(a)} \sum_{i=1}^{N_a^{(\epsilon)}} \epsilon_{ab_i} P_{n_{b_i} l_{b_i} j_{b_i}}(r) \\
 &\quad + r \sum_{i=1}^{N_a^{(z)}} z_a(b_i) \left[\left(\frac{d}{dr} - \frac{\kappa_{b_i}}{r} \right) Q_{n_{b_i} l_{b_i} j_{b_i}}(r) - \left(\frac{V_{\text{nuc}}(r)}{c} \right) P_{n_{b_i} l_{b_i} j_{b_i}}(r) \right].
 \end{aligned} \tag{4-18}$$

It is in the determination of the coefficients $x_a^{(k)}(bcd)$, $y_a^{(k)}(bc)$ and $z_a(b)$ that the MCDF procedure is applied. We use a variational functional defined by the weighted energies

$$\begin{aligned}
 W^{\text{DC}} &= \sum_{i=1}^{n_L} w_i E_{\Gamma_i}^{\text{DC}} / \sum_{i=1}^{n_L} w_i, \\
 &= \sum_{i=1}^{n_L} w_i \sum_{r,s=1}^{n_c} c_{r\Gamma_i} c_{s\Gamma_i} H_{rs} / \sum_{i=1}^{n_L} w_i \equiv \sum_{r,s=1}^{n_c} d_{rs} H_{rs};
 \end{aligned} \tag{4-19}$$

variation with respect to one pair of radial functions, $P_{n_a l_a j_a}(r)$ and $Q_{n_a l_a j_a}(r)$, subject to the boundary conditions (4-16) produces one pair of equations (4-15), and determines all coefficients, $x_a^{(k)}(bcd)$, $y_a^{(k)}(bc)$ and $z_a(b)$, in (4-18). Lagrange multipliers, ϵ_{ab} , are introduced to enforce Eqs. (4-17). The generalised occupation number of an orbital is $\bar{q}(a)$, given by $\sum_{r=1}^{n_c} d_{rr} q_r(a)$; here $q_r(a)$ is the number of electrons in subshell $(n_a l_a j_a)$ in CSF set $[\gamma_r J_r^{P_r}]$.

Equations (4-14) and (4-15) are simultaneously solved using an SCF procedure:

1. The coefficients d_{rs} in (4-19) are calculated from a set of mixing coefficient vectors $\tilde{c}_{\Gamma_i}^{\text{est}}$, $i = 1, \dots, n_L$.
2. The functions $\mathcal{Y}_a(r)$, $\mathcal{X}_a^{(P)}(r)$ and $\mathcal{X}_a^{(Q)}(r)$ in Eq. (4-18) can then be calculated from a set of radial functions $P_{n_a l_a j_a}^{\text{est}}(r)$, $Q_{n_a l_a j_a}^{\text{est}}(r)$, $a = 1, \dots, n_w$.
3. Equations (4-15) are solved using this potential to obtain a new set of radial functions $P_{n_a l_a j_a}^{\text{new}}(r)$, $Q_{n_a l_a j_a}^{\text{new}}(r)$, $a = 1, \dots, n_w$.
4. An improved estimated set of radial functions is obtained from the transformation $[P_{n_a l_a j_a}^{\text{est}}(r), Q_{n_a l_a j_a}^{\text{est}}(r)] \rightarrow (1 - \eta_a)[P_{n_a l_a j_a}^{\text{new}}(r), Q_{n_a l_a j_a}^{\text{new}}(r)] + \eta_a[P_{n_a l_a j_a}^{\text{est}}(r), Q_{n_a l_a j_a}^{\text{est}}(r)]$, where $0 \leq \eta_a < 1$ are damping or accelerating factors. If the improved estimated set of orbitals agrees to within a specified tolerance with the original estimated set, convergence has been achieved. If not, steps 5, 6 and 1 – 4 are executed again.

5. Equation (4-14) is solved using the Hamiltonian obtained with the improved estimated radial functions to calculate a new estimated set of mixing-coefficient vectors $\tilde{c}_{\Gamma_i}^{\text{new}}, i = 1, \dots, n_L$.
6. An improved estimated set of mixing coefficient vectors is obtained from the transformation $\tilde{c}_{\Gamma_i}^{\text{est}} \rightarrow (1 - \xi_i) \tilde{c}_{\Gamma_i}^{\text{new}} + \xi_i \tilde{c}_{\Gamma_i}^{\text{est}}$, where $0 \leq \xi_i < 1$ are also damping or accelerating factors.

The Lagrange multipliers ϵ_{aa} can be interpreted as approximate electron removal energies only in the average level (AL) approximation, when $n_L = n_c$. This is defined by the choice

$$d_{rs} \equiv \begin{cases} (2J_r + 1) / \sum_{t=1}^{n_c} (2J_t + 1) & \text{if } r = s, \\ 0 & \text{otherwise.} \end{cases} \quad (4-20)$$

We are then effectively optimising on the trace of the full Dirac-Coulomb Hamiltonian matrix (with one element for each value of M) which is invariant under the orthogonal transformation which diagonalises it. Steps 5 and 6 are then redundant.

The absolute difference, $|\epsilon_i - \epsilon_j|$ between a pair of Lagrange multipliers can be interpreted as the energy of the photon that is exchanged in the transverse interaction (2-5). Running GRASP² in the AL mode for Ar^{16+} , and diagonalizing the matrix $\tilde{H}^{\text{DC}} + \tilde{H}^{\text{trans}}$, one obtains the approximate ASFs and energies

$$\begin{aligned} |(00000000.00 \text{ cm}^{-1}) 1 0^+ &= 0.9999 |1s_{1/2}^2 0^+ \rangle - 0.0166 |1s_{1/2} 2s_{1/2} 0^+ \rangle, \\ |(25022573.82 \text{ cm}^{-1}) 2 1^+ &= |1s_{1/2} 2s_{1/2} 1^+ \rangle, \\ |(25175203.93 \text{ cm}^{-1}) 2 0^- &= |1s_{1/2} 2p_{1/2} 0^- \rangle, \\ |(25180420.69 \text{ cm}^{-1}) 2 1^- &= 0.8819 |1s_{1/2} 2p_{1/2} 1^- \rangle - 0.4715 |1s_{1/2} 2p_{3/2} 1^- \rangle, \\ |(25192331.99 \text{ cm}^{-1}) 2 0^+ &= 0.9999 |1s_{1/2} 2s_{1/2} 0^+ \rangle + 0.0166 |1s_{1/2}^2 0^+ \rangle, \\ |(25202522.72 \text{ cm}^{-1}) 2 2^- &= |1s_{1/2} 2p_{3/2} 2^- \rangle, \\ |(25312695.15 \text{ cm}^{-1}) 2 1^- &= 0.8819 |1s_{1/2} 2p_{3/2} 1^- \rangle + 0.4715 |1s_{1/2} 2p_{1/2} 1^- \rangle. \end{aligned} \quad (4-21)$$

The excited states' energies in (4-21) are all too high (cf. (4-10)) by amounts varying from $\approx 9000 - 14000 \text{ cm}^{-1}$. This is largely due to the greater sensitivity of the lowest-lying state to correlation effects. Note, however, that the fine-structure splittings between the lowest three states J^- are incorrect by only $\approx 400 \text{ cm}^{-1}$: high quality fine-structure splittings are characteristic of AL calculations. The remaining discrepancy is due to physical effects that are not accounted for — as described above in the last paragraph of section 2. For many purposes, however, the results of such AL calculations are quite acceptable. GRASP² AL calculations with $n_c \approx 800$ are routinely performed at Oxford.

Consider the problem of improving the estimate of the $|10^+\rangle$ state in Ar^{16+} . As Fischer /23/ has shown, the exact ground-state eigenfunction of a Hamiltonian for a two-electron atom is obtained in the limit $n_{\text{max}} \rightarrow \infty$ of

$$|10^+\rangle = \sum_{n=1}^{n_{\text{max}}} \sum_{j=1/2}^{n-1/2} |(nlj)^2 0^+\rangle. \quad (4-22)$$

The optimal level (OL) method — which allows us to improve the energy of a single level at the cost of obtaining poorer estimates of all other levels included in the calculation —

Table 1. A sequence of GRASP² OL calculations together with an extrapolation procedure can be used to estimate eigenenergies to high precision: we obtain $E_{\text{exact}}^{\text{DC}} = -68\,967\,940 \pm 10 \text{ cm}^{-1}$ and $E_{\text{exact}}^{\text{DC+Breit}} = -68\,953\,000 \pm 100 \text{ cm}^{-1}$.

n_{max}	$E_{n_{\text{max}}}^{\text{DC}}$	E_{∞}^{DC}	$E_{n_{\text{max}}}^{\text{DC+Breit}}$	$E_{\infty}^{\text{DC+Breit}}$
1	-68 957 877.711	-68 957 877.711	-68 941 637.091	-68 941 637.091
2	-68 965 935.542	-68 967 086.661	-68 950 377.686	-68 953 149.956
3	-68 967 260.013	-68 967 920.028	-68 951 896.372	-68 952 722.269
4	-68 967 639.013	-68 967 953.165	-68 952 373.162	-68 952 826.318
5	-68 967 782.962	-68 967 941.925	-68 952 579.372	-68 952 879.571
6	-68 967 847.974	-68 967 935.814	-68 952 689.461	-68 952 929.859

is obtained by setting $n_L = 1$ in Eq. (4-19). This is clearly the method of choice for the problem at hand. We carry out a series of OL calculations with $n_{\text{max}} = 1, \dots, 6$; the results are listed in column 2 of Table 1. The differences between consecutive pairs of entries are fitted to a polynomial with terms $a_k/(n-1/2)^{4+k}/24/$. Summing the polynomial over all values of $n > n_{\text{max}}$ yields the entries in column 3 of Table 1.

Because it is now impossible to interpret the Lagrange multipliers ϵ_{aa} as one-electron removal energies, we are constrained to use Eq. (2-6) — which is independent of the energy of the exchanged photon — to compute effects of higher order. In addition, because we are using perturbation methods, it is necessary to go beyond the expansion (4-22) and include all possible CSFs in a systematic manner; the appropriate expansion is

$$|1\,0^+\rangle = \sum_{n_1, n_2=1}^{n_{\text{max}}} \sum_{j=1/2}^{\min(n_1, n_2)-1/2} |(n_1\,l\,j)(n_2\,l\,j)\,0^+\rangle. \quad (4-23)$$

In column 4 of Table 1 we exhibit the results of the corresponding sequence of computations. The terms of the fitting polynomial are now of the form $a_k/(n-1)^{3+k}$. Extrapolated results are listed in column 5.

Extended AL (EAL) results are obtained when the weights $(2J_r + 1)$ in Eq. (4-20) are replaced by w_r chosen by the user. Extended OL (EOL) calculations are obtained when $1 < n_L < n_c$ in Eq. (4-19).

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References

- /1/ GRANT, I.P., and QUINEY, H.M., *Adv. At. Mol. Phys.* **23** (1988) 37.
- /2/ DIRAC, P.A.M., *Proc. Roy. Soc.* **A117** (1928) 610.
- /3/ BERESTETSKII, V.B., LIFSHITZ, E.M., and PITAEVSKII, L.P., *Relativistic Quantum Theory*, Pergamon, Oxford, 1971.
- /4/ BREIT, G., *Phys. Rev.* **34** (1929) 553; *ibid.* **36** (1930) 383; *ibid.* **39** (1932) 616.
- /5/ GAUNT, J.A., *Proc. Roy. Soc. (London)* **A122** (1929) 513.
- /6/ GRANT, I.P., pp. 1-71 in *Methods in Computational Chemistry*, Vol. 2, (ed. S. Wilson), Plenum, New York, 1988.
- /7/ GRANT, I.P., *Comput. Phys. Commun.* **4** (1972) 377. Erratum: *ibid.* **14** (1978) 311.
- /8/ GRANT, I.P., *Comput. Phys. Commun.* **5** (1973) 263. Erratum: *ibid.* **13** (1978) 429.
- /9/ GRANT, I.P., *Comput. Phys. Commun.* **11** (1976) 397. Erratum: *ibid.* **14** (1978) 312.
- /10/ PYPER, N.C., GRANT, I.P., and BEATHAM N., *Comput. Phys. Commun.* **15** (1978) 387.
- /11/ CHANG, J.J., *Comput. Phys. Commun.* **7** (1974) 225.
- /12/ McKENZIE, B.J., GRANT, I.P., and NORRINGTON, P.H., *Comput. Phys. Commun.* **21** (1980) 233.
- /13/ BEATHAM, N., GRANT, I.P., McKENZIE, B.J., and PYPER, N.C., *Comput. Phys. Commun.* **18** (1979) 245.
- /14/ GRANT, I.P., and McKENZIE, B.J., *J. Phys. B: At. Mol. Phys.* **13** (1980) 2671.
- /15/ GRANT, I.P., McKENZIE, B.J., NORRINGTON, P.H., MAYERS, D.F., and PYPER, N.C., *Comput. Phys. Commun.* **21** (1980) 207.
- /16/ DYALL, K.G., GRANT, I.P., JOHNSON, C.T., PARPIA, F.A., and PLUMMER, E.P., *Comput. Phys. Commun.* **55** (1989) 425.
- /17/ DYALL, K.G., *Comput. Phys. Commun.* **39** (1986) 141.
- /18/ BAR-SHALOM, A., and KLAPISCH, M., *Comput. Phys. Commun.* **50** (1988) 375.
- /19/ BURKE, P.G., *Comput. Phys. Commun.* **1** (1970) 241. Erratum: *ibid.* **2** (1971) 173.
- /20/ FISCHER, C.F., *Comput. Phys. Rep.* **3** (1986) 273.
- /21/ RAMANA, M.V., RAJAGOPAL, A.K., *Adv. Chem. Phys.* **54** (1983) 231.
- /22/ DRAKE, G.W.F., *Can. J. Phys.* **66** (1988) 586.
- /23/ FISCHER, C.F., *The Hartree-Fock Method for Atoms*, Wiley, New York, 1977.
- /24/ PARPIA, F.A., and GRANT, I.P., *J. Phys. B: At. Mol. Opt. Phys.* **23** (1990) 211.