

## Current Developments in the Relativistic Quantum Mechanics of Atoms and Molecules\*

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### Abstract

Current work in relativistic quantum mechanics by the author and his associates focusses on four topics: atomic structure theory using the GRASP package (Dyall 1986); extension of GRASP to handle electron continuum processes; the relation of quantum electrodynamics and relativistic quantum mechanics of atoms and molecules; and development of methods using finite basis set expansions for studying electronic structure of atoms and molecules. This paper covers only the last three topics, giving emphasis to growing points and outstanding difficulties.

### 1. Introduction

The ease with which quantitative predictions in atomic spectroscopy can be made when relativistic effects must be taken into account has increased enormously in recent years as codes like those of Desclaux (1975) and Grant *et al.* (1980) have become more widely distributed. Dyall (1986, present issue p. 667) discusses some aspects of current developments of this kind, giving some idea of our expectations of the new GRASP system (Dyall *et al.* 1986). In this paper, three developments related to the preceding work are considered. Section 2 will outline an attempt to embed relativistic atomic structure theory in the manner of GRASP into quantum electrodynamics (QED) in a way which resolves many of the puzzles and contradictions receiving discussion in the contemporary literature. This will justify the traditional methods of relativistic atomic structure, but will leave several open questions to tax the ingenuity of theorists in the next few years. Section 3 will briefly describe projected developments in the theory of electron continuum processes in heavy atoms where relativistic effects are important in low energy electron collisions, in photo-excitation and -ionisation, and related processes. Finally, in Section 4 recent progress with the use of the algebraic basis set approach in atoms and its implications for the development of *ab initio* quantum chemistry calculations for molecules containing heavy elements when relativistic effects must be taken into account will be discussed.

### 2. Relativistic Atomic Structure Theory as an Approximation to QED

Quantitative methods of making quantum mechanical predictions for atoms and molecules generally rely on an orbital approximation. Whilst this can be taken

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for granted in nonrelativistic quantum mechanics, the description of an orbital as the product of a spatial wavefunction multiplied by a purely harmonic time-varying amplitude carries severe restrictions in relativistic quantum mechanics. Indeed it seems essential to assume that the potential energy of the electron is time-independent in a given reference frame. If the forces are electromagnetic, we need a pure electrostatic potential, so that one is driven to the conventional *fixed nucleus* approximation in which the electronic orbital spinors have the form

$$\psi(x) = \psi_\epsilon(x) \exp(-i \epsilon t), \quad x = (ct, \mathbf{x}), \tag{1}$$

and satisfy the Dirac equation

$$h\psi_\epsilon(x) = \epsilon\psi_\epsilon(x), \tag{2}$$

where in conventional notation (Grant 1970)

$$h \equiv c\alpha \cdot p + (\beta - 1)c^2 + U(x) \tag{3}$$

and  $U(x)$  is the (attractive) potential energy of the electron in the field of some model charge distribution. For example, if  $U(x)$  corresponds to an unshielded point nucleus of charge  $Z$ , then  $U(x) = -Z/r$  where  $r = |x|$ . [We use Hartree atomic units throughout, and conventional Dirac matrices (Grant 1970).] In any other inertial frame of reference, the four-potential will include magnetic vector potential terms as well as electrostatic terms, and  $\psi(x)$  will no longer be factorisable as in (1).

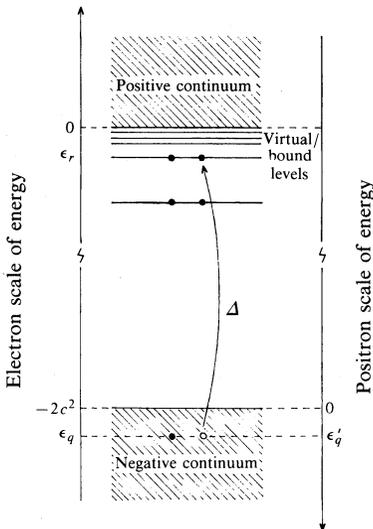


Fig. 1. Diagram showing the formation of a positron of energy  $\epsilon'_q$  relative to rest, along with an electron of energy  $\epsilon_r$ , by excitation from a lower continuum state of energy  $\epsilon_q$ .

Once we have fixed our potential  $U(x)$ , which we take implicitly to have the form of a typical atomic potential energy function, we can develop QED in the Furry (1951) bound-interaction picture. First we consider an assembly of non-interacting

electrons. The electron-positron field amplitude can be expressed in the form

$$\psi(x) = \sum_p^{(+)} b_p \psi_p(x) \exp(-i \epsilon_p t) + \sum_q^{(-)} d_q^\dagger \psi_q(x) \exp(-i \epsilon_q t), \quad (4)$$

where  $\psi_p(x)$  and  $\psi_q(x)$  are solutions of (2) corresponding to energy eigenvalues  $\epsilon_p$  and  $\epsilon_q$  respectively. The formal sums run over both continuum solutions  $\epsilon_p > 0$ ,  $\epsilon_q < -2c^2$  and discrete (square normalisable) solutions,  $-2c^2 < \epsilon_p < 0$ ; for simplicity we treat the continuum solutions formally as discrete in energy, as the formalities of dealing with a continuous distribution of energy do nothing to help one's understanding of the physics. The operators  $b_p$  and  $d_q^\dagger$  are, respectively, destruction operators for the 'positive' energy (electron) states, and creation operators for 'negative' energy positron states ('holes' in the lower continuum, see Fig. 1), satisfying the anticommutation rules

$$\begin{aligned} \{b_p, b_{p'}\} &= \{b_p^\dagger, b_{p'}^\dagger\} = \{d_q, d_{q'}\} = \{d_q^\dagger, d_{q'}^\dagger\} \\ &= \{b_p, d_q^\dagger\} = \{b_p^\dagger, d_q\} = 0, \\ \{b_p, b_{p'}^\dagger\} &= \delta_{pp'}, \quad \{d_q, d_{q'}^\dagger\} = \delta_{qq'}. \end{aligned} \quad (5)$$

The number of particles associated with orbital  $p$  is the expectation of the operator  $n_p = b_p^\dagger b_p$  taking the values 0 or 1, and  $n_q = d_q^\dagger d_q$  gives the number of electrons in the positron state  $q$ . This is just what we require for Fermi particles obeying Pauli's exclusion principle. The *ground state* of the system in which we are interested has  $N$  electrons ( $\sum_p^{(+)} n_p = N$ ) and *no* positrons ( $\sum_q^{(-)} n_q = 0$ ). Now the total energy in this formalism is

$$E = \sum_p^{(+)} n_p \epsilon_p + \sum_q^{(-)} n_q \epsilon_q, \quad (6)$$

so that the ground state energy is

$$E_0 = \sum_{\text{occ}}^{(+)} n_p \epsilon_p, \quad \sum_{\text{occ}}^{(+)} n_p = N, \quad \sum_q^{(-)} n_q = 0.$$

The total charge in this model can be written as the expectation of the operator  $Q$ , proportional to the  $\mu = 0$  component of the total *charge-current vector*

$$J^\mu = -ec \int : \tilde{\psi}(x) \gamma^\mu \psi(x) : d\tau. \quad (7)$$

The colons denote *normal order* of the creation-destruction operators: in this convention, all such operators are ordered so that destruction operators (for electrons or positrons) appear to the right of creation operators, any interchanges involved being performed as if all the anticommutators (5) vanish. Thus  $E$  in (6) is already in normal form, so that the *vacuum* ( $n_p = 0$ ,  $n_q = 0$  for all  $p$  and  $q$ ) has zero energy.

Using (4), assuming all amplitudes  $\psi_p(x)$  and  $\psi_q(x)$  are orthonormal, we find

$$Q = J^0/c = -e \left( \sum_p^{(+)} n_p - \sum_q^{(-)} n_q \right); \quad (8)$$

this ensures that the vacuum has zero net charge. Here  $Q$  is a *constant of the motion*, so that if we start with  $N_e$  electrons and  $N_p = 0$  positrons, charge conservation will allow mixing of this state with  $N_e + 1$  electrons and 1 positron, and so on. Since each state can only accommodate one electron or positron, the *excitation energy* is  $\Delta = \epsilon_r + \epsilon'_q + 2c^2$  (see Fig. 1). For normal atoms,  $\Delta$  is at least of order 1 MeV; even for uranium,  $Z = 92$ , the lowest 'positive energy' state, 1s, has  $\epsilon_{1s} \approx -115$  keV. It requires a *super-critical* nuclear charge  $Z \approx 173$  to make  $\epsilon_{1s} \approx -2c^2$ . Thus for most purposes, the energy required to excite an electron-positron pair is too much to affect the low energy processes of most interest in atomic and molecular physics, though we can expect them to contribute beyond the first order in perturbation theory.

The formalism just described gives mathematical form to Dirac's hole theory (Dirac 1930) for stabilising the hydrogen ground state. This is, of course, well known. What is usually omitted in the discussion of the stability of *many-electron atoms*, when the electron-electron interaction is included (Sucher 1980), is that the *same* argument justifies their stability and that the excitation energy needed to create one or more electron-positron pairs is large. The square integrability condition on bound orbital spinors imposes strict boundary conditions at the nucleus and at large distances (Grant 1982), and implies that bound states can only occur for energy eigenvalues  $\epsilon_p$  in the interval  $-2c^2 < \epsilon_p < 0$ . Thus physical instability of atomic models based on these principles is not a problem if one accepts hole or positron theory. The bound electrons see a potential determined only by the physical atomic charge distribution itself, as in nonrelativistic theory, and it is sufficient to ignore 'negative energy' states completely in a first approximation.

So far, we have not put interactions into the mathematics. In QED the free electron-positron Dirac field and the Maxwell field can be coupled by the interaction Lagrangian density

$$L_{\text{int}}(x) = -j^\mu(x) A_\mu(x), \quad (9)$$

where  $A_\mu(x)$  is a *quantised* four-potential. The development of QED from this standpoint by using perturbation theory and Feynman diagrams is more or less standard (see e.g. Björken and Drell 1964; one of many texts on the subject). The bound state energies can be obtained from the level shift formula (Gell-Mann and Low 1951) for a system of  $N$  electrons, with *no* free positrons or photons. Expanding in a perturbation series to *second order* in  $L_{\text{int}}$  gives an effective atomic Hamiltonian (the *standard model*)

$$H = H_0 + V, \quad (10)$$

where

$$H_0 = \sum_p^{(+)} b_p^\dagger b_p \epsilon_p,$$

$$V = V_1 + V_2,$$

and where

$$V_1 = \sum_{p,q}^{(+)}: b_p^\dagger b_q : \langle p | -U(x) - Z/r | q \rangle,$$

$$V_2 = \frac{1}{2} \sum_{p,q,r,s}^{(+)}: b_p^\dagger b_q^\dagger b_s b_r : \langle pq | v | rs \rangle.$$

Here, we take the nucleus to be a fixed point charge, producing an unquantised external field, so that  $V_1$  is a counter term inserting  $-Z/r$  into the zero-order Dirac operator and removing  $U(x)$ , whilst  $V_2$  is the covariant electron-electron interaction in the Coulomb gauge

$$v(x_1, x_2) = 1/R + T(x_1, x_2), \quad R = |x_1 - x_2|, \quad (11)$$

the sum of the instantaneous Coulomb repulsion and the transverse photon (magnetic retarded) interaction  $T(x_1, x_2)$  (Grant 1983). For low energy processes  $T(x_1, x_2)$  can be approximated by Breit's (1930, 1932) interaction

$$B(R) = -\frac{1}{2R} \left( \alpha_1 \cdot \alpha_2 + \frac{(\alpha_1 \cdot R)(\alpha_2 \cdot R)}{R^2} \right); \quad (12)$$

we note that this is not appropriate for interactions in which orbital energy differences are comparable with  $c^2$  (in a.u.) for which the full expression (11) is needed. This model is physically stable, for the same reason as before.

There are several omissions from the standard model:

(a) QED introduces divergent, but renormalisable, self-energy terms which should be included in the perturbation series. The *electron self-energy*, responsible for the major part of the Lamb shift of atomic energy levels, has only been calculated rigorously for the hydrogenic case  $U = -Z/r$  (see e.g. Mohr 1974, 1975, 1982). A screened hydrogenic approximation is normally used in current many-electron codes (Desclaux 1975; McKenzie *et al.* 1980), and a method suitable for the more general model (10) remains to be developed. The nuclear charge distribution polarises the photon vacuum, leading to a short-range modification of the nuclear Coulomb potential; this is straightforward to approximate (McKenzie *et al.* 1980).

(b) *Nuclear motion* has been neglected. In nonrelativistic quantum mechanics for isolated atoms, the nuclear motion is accounted for by transforming to the atomic centre-of-mass (Condon and Shortley 1951; Ch. XVIII). To a first approximation, the centre-of-mass motion decouples, the effect being to multiply the electron mass  $m$  by a factor  $(1 + m/M)^{-1}$ ,  $M$  being the nuclear mass. This affects the conversion of atomic to laboratory units. The residual coupling, or mass polarisation term,

$$S = \frac{1}{M} \sum_{i \neq j} p_i \cdot p_j, \quad (13)$$

gives rise to a small correction, usually considered along with the effect of isotopic variations in the nuclear charge distribution as part of the *isotope shift* of atomic energy levels.

The relativistic theory is less complete. Approximations can be developed for the hydrogen atom using either the Bethe-Salpeter equation (Salpeter and Bethe 1951;

Gell-Mann and Low 1951) or a more empirical approach (Grotch and Yennie 1969). These methods give the nonrelativistic result in lowest order, but it is not clear what to do for higher-order corrections in many-electron atoms. What is worse is that the fixed nucleus approximation forces us to accept the *Born–Oppenheimer approximation* for molecules. All molecular calculations in relativistic quantum theory have so far used this assumption, and its relaxation is a major unsolved problem for theory.

(c) The nucleus is not an infinitely massive point charge, but has a finite size charge distribution and, generally, has nonzero electric and magnetic multipole moments which give hyperfine structure in atomic spectra. In atomic structure calculations one can model the nuclear charge as a simple spherically symmetric distribution without difficulty. Whilst the parameters are often known from experiment (Barrett and Jackson 1977), it is not always clear that they are appropriate for atomic structure calculations, and this is often the major contributor to the numerical uncertainty in the position of X-ray levels in heavy atoms. Hyperfine interactions can be included later as a perturbation.

If we accept the *standard model*, despite its shortcomings, we have still to choose  $U(x)$ . There are several possibilities, all in common use:

(i) Choose  $U(x) = -Z/r$ , where the orbitals are hydrogenic spinors. This starting point for perturbation theory has traditionally been used by groups in the U.S.S.R. (Safronova and Rudzikas 1976).

(ii) Choose  $U(x)$  to be a model potential with adjustable parameters (Luc-Koenig 1972, 1976; Klapisch *et al.* 1977).

(iii) Choose  $U(x)$  so that  $\langle \phi_0 | V | \phi_0 \rangle = 0$ , where  $|\phi_0\rangle$  is the ground state of the system and  $V$  is the perturbation component of (10). This is the Dirac–Fock (DF  $\equiv$  relativistic Hartree–Fock) prescription used in GRASP, a system which admits further multiconfigurational approximations (MCDF –OL, –AL, –EOL, –EAL) in the same vein (Dyall *et al.* 1986).

(iv) Choose  $U(x)$  to satisfy the  $g$ -Hartree equations (Dietz *et al.* 1982) which account in a variational manner for part of the higher-order perturbations in QED.

We note that none of these methods leads to any practical ambiguities. The self-consistent-field (SCF) problem (iii) or (iv), in which the potential  $U(x)$  is defined with respect to a set of *occupied bound orbitals* (satisfying the usual boundary conditions), is mathematically well-defined. We present some numerical evidence below. There is no need, within the orbital approximation, to use the projection operators advocated by Sucher (1980) as it is quite clear which orbitals are physically relevant in any practical problem.

### 3. Electron–Continuum Calculations

The use of the  $R$ -matrix method (Burke and Robb 1975) for the calculation of low-energy electron-scattering cross sections, photo-excitation and -ionisation, Auger transitions and dielectronic recombination rates has become commonplace over the last few years. Programs are available for light atoms, when  $LS$  coupling applies and the Hartree–Fock method can be used (Berrington *et al.* 1978), but this is not adequate when the atomic number increases. One approach is to include relativistic effects

through the Breit–Pauli approximation and to transform to intermediate coupling (Scott and Taylor 1982), but a more satisfactory approach in the long term must be based on the standard model Hamiltonian (10).

It proves relatively straightforward to devise a numerical method for this purpose (Chang 1975, 1977; Norrington and Grant 1981, 1985). The space surrounding the target atom is divided into two regions: an inner one, in which the  $N$  electrons of the target and the incident electron are treated on the same footing, and an outer one in which the scattered electron sees a much simpler long-range effective potential. The target core defines an effective potential for a set of basis orbital spinors having finite amplitudes on the  $R$ -matrix boundary,  $r = a$ , and satisfying the condition (Norrington and Grant 1981)

$$2c Q(a)/P(a) = (b + \kappa)/a, \quad (14)$$

where  $Q$  and  $P$  are, respectively, the small and large radial components of the orbital basis spinor,  $\kappa$  is the angular symmetry quantum number, and  $b$  is a constant (usually set to zero). This reduces correctly to the standard nonrelativistic prescription  $P'(a)/P(a) = b/a$  (Berrington *et al.* 1978), as the speed of light  $c$  is allowed to become infinite. Apart from the use of the boundary condition (14), the problem is now virtually identical to a multiconfigurational bound state calculation in the region  $r < a$ . Our current results have been obtained with an inefficient code based on the RMATRIX package (Berrington *et al.* 1978); however, in collaboration with P. H. Norrington (now at Queen's University, Belfast) we are constructing what we intend to be a much more efficient scheme using GRASP modules and organisation (Johnson and Grant 1986).

The region  $r > a$  is essentially one in which nonrelativistic dynamics can be used. The effective nonrelativistic amplitude  $\hat{P}_i(r)$  for the scattered electron in the  $i$ th channel satisfies an equation of the form

$$\hat{P}_i'' + \left( k_i^2 - \frac{l_i(l_i+1) - Z^2/c^2}{r^2} + \frac{2z_i}{r} \right) \hat{P}_i + \sum_k \sum_j W_{ij}^k \frac{\hat{P}_j}{r^{k+1}} \approx 0, \quad (15)$$

where  $k_i^2 = 2e_i(1 + e_i/2c^2)$  is the *relativistic* squared momentum corresponding to energy  $e_i > 0$ ,  $l_i$  is the orbital angular momentum quantum number,  $z_i = Z(1 + e_i/c^2)$  is an energy-dependent effective charge reducing to  $Z$  in the nonrelativistic limit, and the  $W_{ij}^k$  coefficients, which arise from channel coupling, also contain relativistic corrections of order  $1/c^2$ . Clearly, relativistic corrections can be neglected for most purposes, so that standard nonrelativistic packages for solving (15) in the outer region can be used unmodified. This means that the matching of solutions on  $r = a$ , the subsequent evaluation of  $K$ -matrices and eigenphase shifts, the identification of resonances, and the calculation of other quantities which permit one to evaluate the required cross sections, can exploit existing software embodied in RMATRIX.

Norrington and Grant (1981) reported a first calculation for electron scattering from  $\text{Ne}^+$  which gave good agreement with nonrelativistic calculations using RMATRIX. Including orbital angular momenta  $l \leq 8$ , RMATRIX required 90 basis functions and 11 000 radial integrals to construct the Hamiltonian, whereas the relativistic calculation introduced 170 basis functions and required 60 000 radial integrals, needing *five* times

as much computer time. These tests convinced us of the need to construct a more efficient code. We have recently (Norrington and Grant 1985) described a similar calculation on electron scattering from Fe XXIII at energies up to 25 Ryd (1 Ryd = 13.605 eV). This gave good agreement with the Breit–Pauli intermediate coupling results of Scott and Burke (1980) at a similar cost in CPU time. The extra work in calculating Dirac basis functions accounts for only a small part of the total time of this calculation.

#### 4. Basis Set Calculations of Bound States of Atoms and Molecules

The idea of using finite dimensional sets of basis functions has permitted the development of many of the methods currently used in quantum chemistry. When the first attempts were made by Kim (1967) and later by Kagawa (1975, 1980) to perform *atomic* DF and MCDF calculations using STO basis sets of functions proportional to  $r^\gamma \exp(-\zeta r)$  where  $\gamma$  is not an integer, the results seemed acceptable, if a little less accurate than corresponding calculations using finite difference techniques. However, the first relativistic calculations using more conventional basis sets for both atoms and molecules often gave very poor results: The computed energy levels were not necessarily variational upper bounds, as expected from nonrelativistic experience, and some of the levels appeared to have no connection with the physical problem. Kutzelnigg (1984), reviewing the situation in June 1982, listed some 15 different suggestions to abolish the spurious states, and to ensure that the method produced an upper bound, but he was not able to give an unequivocal recommendation in favour of any one suggestion.

Our own work on this problem began with a paper (Grant 1982) analysing the convergence pattern exhibited by basis set calculations in hydrogenic atoms by Drake and Goldman (1981), who used  $N$ -dimensional sets of functions  $\exp(-\mu r) r^{\gamma+j-1}$ , where  $\gamma$  is the (non-integer) Coulomb cusp exponent,  $\gamma = (\kappa^2 - Z^2/c^2)^{1/2}$ ,  $\mu$  is a variational parameter, and  $j = 1, 2, \dots, N$ . They found that the eigenvectors fell into two classes:  $N$  of them approximated by the lower continuum, having eigenvalues below  $-2c^2$  (using our choice of energy zero and units); some of the remaining  $N$  gave eigenvalues which were upper to the exact bound hydrogenic eigenvalues in  $-2c^2 < \epsilon < 0$ , whilst the residue represented square-integrable approximations to positive energy continuum states with  $\epsilon > 0$ . The bound state eigenvalues appeared to converge smoothly from above onto the exact analytical values as  $N$  increased.

The analysis by Grant (1982) examined the role of boundary conditions in defining bound states of the Dirac hydrogenic problem. The variational equations for the reduced Dirac (radial) equation for a single electron in a Coulomb field reduce to the  $2N \times 2N$  matrix eigenvalue equation

$$\begin{bmatrix} V & c\Pi_\kappa \\ c\Pi_\kappa^\dagger & -2c^2S + V \end{bmatrix} \begin{bmatrix} p \\ q \end{bmatrix} = \epsilon \begin{bmatrix} S & p \\ S & q \end{bmatrix}, \quad (16)$$

where  $p$  and  $q$  are  $N$ -rowed column vectors, and the sub-matrices on the left are  $N \times N$ ;  $V$  is the matrix of the potential with respect to the basis set,  $S$  is the Gram (overlap) matrix, and  $\Pi_\kappa$  is the matrix of the operator  $(-d/dr + \kappa/r)$ , with  $\Pi_\kappa^\dagger$  its matrix adjoint. By eliminating the vector  $q$ , the coefficients defining the small component as a linear combination of basis functions, we get a Schrödinger-like

pseudo-eigenvalue equation

$$\{T' + V + K(\epsilon)\}p = \epsilon Sp, \quad (17)$$

where

$$T' = \frac{1}{2} \Pi_{\kappa} S^{-1} \Pi_{\kappa}^{\dagger}, \quad K(\epsilon) = O(1/c^2).$$

By *hypothesising* that  $T'$  could be replaced by  $T$ , the matrix of  $\{-\frac{1}{2}d^2/dr^2 + l(l+1)/r^2\}$ , we see first that (17) is just the Schrödinger equation in the nonrelativistic limit  $c \rightarrow \infty$ . We could also show that if  $V$  had a sufficiently small spectral radius, and the hypothesis on  $T$  was valid,  $N$  of the (relativistic) eigenvalues should lie in the half-line  $\epsilon > -2c^2$ , and  $N$  in the half-line  $\epsilon < -2c^2$ . This, in conjunction with an eigenvalue separation result analogous to the theorem of Hylleraas and Undheim (1930) and MacDonald (1933), was enough to explain the observations of Drake and Goldman (1981).

Clearly, greater precision was needed. The first step was to examine the following question: If  $A$  and  $B$  are two quantum mechanical operators, and  $A$  and  $B$  are their matrix representations with respect to a finite non-orthogonal basis set of dimension  $N$  with overlap matrix  $S$ , if the operator  $C = AB$  has matrix representation  $C$ , when does  $C = AS^{-1}B$ ? Dyall *et al.* (1984a) showed that  $C \neq AS^{-1}B$  unless  $B$  and  $A^{\dagger}$  both map the chosen finite basis set into the *same* finite subset of their respective ranges. Thus  $T' = \frac{1}{2} \Pi_{\kappa} S^{-1} \Pi_{\kappa}^{\dagger}$  is not in general equal to  $T$ . However, we can force equality of  $T'$  and  $T$ , by using a *different* basis set for the large and small components such that each *large component* basis function  $\pi_i(r)$  has an associated *small component* basis function  $\rho_i(r)$ , related by

$$\rho_i(r) = (d/dr + \kappa_i/r)\pi_i(r), \quad i = 1, 2, \dots, N \quad (18)$$

up to a normalisation factor. It is easy now to check that

$$T = \frac{1}{2} \Pi_{\kappa} S_{\rho\rho}^{-1} \Pi_{\kappa}^{\dagger},$$

where  $S_{\rho\rho}$  is the overlap matrix of the set  $\{\rho_i\}$ , ensuring that (17) gives the correct nonrelativistic energy. If we do not make this choice of small component basis function, it is clear that  $T'$  will *always* underestimate the kinetic energy. For in the general three-dimensional case, we are trying to construct the finite matrix equivalent of the operator equality

$$p^2 = (\boldsymbol{\sigma} \cdot \mathbf{p})^{\dagger} (\boldsymbol{\sigma} \cdot \mathbf{p}).$$

The expectation of  $p^2$  with respect to  $\psi$  is

$$\langle \psi | p^2 | \psi \rangle \equiv -\langle (\boldsymbol{\sigma} \cdot \mathbf{p})\psi | (\boldsymbol{\sigma} \cdot \mathbf{p})\psi \rangle = \|(\boldsymbol{\sigma} \cdot \mathbf{p})\psi\|^2, \quad (19)$$

and any expansion of the vector  $(\boldsymbol{\sigma} \cdot \mathbf{p})\psi$  in terms of an arbitrary set of basis functions must give an underestimate of  $\langle \psi | p^2 | \psi \rangle$  unless the basis set is complete in the relevant Hilbert space. Our prescription (18) picks the right finite set of functions to ensure that the equality in (19) holds.

The rest of the analysis is as before, except that the criterion, that the eigenvalues of the modified equation (with each submatrix labelled with the basis sets used in its construction)

$$\begin{bmatrix} V_{\pi\pi} & (c\mathbf{II}_{\kappa})_{\pi\rho} \\ (c\mathbf{II}_{\kappa})_{\pi\rho}^{\dagger} & -2c^2 S_{\rho\rho} + V_{\rho\rho} \end{bmatrix} \begin{bmatrix} p \\ q \end{bmatrix} = \epsilon \begin{bmatrix} S_{\pi\pi} p \\ S_{\rho\rho} q \end{bmatrix} \quad (20)$$

separate into two disjoint sets in the manner reported by Drake and Goldman, becomes

$$\begin{aligned} v_{\min} &= \inf_p (p^{\dagger} V_{\pi\pi} p) / (p^{\dagger} S_{\pi\pi} p) \\ &= \inf_q (q^{\dagger} V_{\rho\rho} q) / (q^{\dagger} S_{\rho\rho} q) \\ &> -2c^2. \end{aligned} \quad (21)$$

This imposes an important restriction on the basis set; thus if we consider the *special case* of a  $2p_{1/2}$  function ( $n = 2, \kappa = +1$ ) for which we use a *single* STO ( $N = 1$ )

$$\pi(r) = K r^2 \exp(-\zeta r), \quad (22)$$

we find

$$\rho(r) = K'(3r - \zeta r^2) \exp(-\zeta r),$$

where  $K$  and  $K'$  are normalising constants. This gives  $v_{\min} = -\frac{2}{3}Z\zeta$ , giving

$$\zeta < \zeta_{\max} = 5.6 \times 10^4 / Z \text{ (bohr}^{-1}\text{)}$$

(1 bohr = 1 a.u. =  $0.529 \times 10^{-10}$  m); a value of  $\zeta$  larger than  $\zeta_{\max}$  would make  $\pi(r)$  in (22) a very contracted function. When  $N > 1$ , an elementary application of Gershgorin's theorem (Wilkinson 1965) shows that the value of  $\zeta_{\max}$  will be somewhat smaller. Thus, if the basis set contains exponents so large that (21) no longer holds, we *may* find eigenvalues below the correct values. This will happen when the strongly negative expectation of the potential is not compensated properly by an appropriately large positive kinetic energy. In fact, the choice (22) for  $2p_{1/2}$  does not have quite the right behaviour near the origin, and we expect to see anomalous behaviour when  $Z$  becomes sufficiently large. The consequences of such behaviour for the choice of basis sets will be examined in a forthcoming paper (Quiney *et al.* 1986).

The first tests on hydrogenic systems fully vindicated this theory. The minimal ( $N = 1$ ) case, using both STO and GTO functions, can be treated analytically (Dyall *et al.* 1984*b*), but we used systematic sequences of even-tempered basis functions for  $N = 2, 3, \dots, 14$  to study convergence with increasing  $N$  (Dyall *et al.* 1984*c*). The next step was to carry out DF calculations on simple closed shell atoms. Quiney *et al.* (1986) give results for the  $1s^2$  system and the  $1s^2 2s^2$  system, some of which are reported in Table 1. As can be seen, the results agree with those computed using the standard GRASP package to about seven significant figures, which we regard as adequate for demonstration purposes. In addition, we have sought confirmation of the view, taken implicitly in Section 2, that there is no need to separate the two parts of the covariant Coulomb interaction (11). Because of the large number of integrals to be calculated, GRASP treats  $T(x_1, x_2)$  as a perturbation, its contribution being added in after a DF calculation, using only the Coulomb repulsion between electron pairs,

has converged. If we use the Breit approximation (12), this is particularly easy to do within the matrix DF method, and we have confirmed (Table 2) that, when  $B(\mathbf{R})$  is used as a perturbation, we get good agreement with GRASP, and that these results are very close to those obtained when  $B(\mathbf{R})$  is included in the SCF iterations. There is no evidence that folklore, suggesting that the Breit interaction will cause the atomic model to destabilise, has any substantial truth.

**Table 1.** Comparison of matrix DF and GRASP solutions for ground states of He-like systems ( $1s^2\ ^1S_0$ ) and Be-like systems ( $1s^2 2s^2\ ^1S_0$ )

Only the electron–electron Coulomb interaction is taken into account; point-nucleus model.

Basis sets:  $\{r \exp(-\zeta_j r) | \zeta_j = \alpha\beta^{j-1}, j = 1, \dots, N\}$

Z	N	$\alpha$	$\beta$	$\nu_{\min}$	Property <sup>A</sup>	Value	
						Matrix DF	GRASP
He-like systems ( $1s^2\ ^1S_0$ )							
2	8	1.05024	1.32634	-34.5	$E_T$	-2.8618134	-2.86181336
					$\epsilon_{1s}$	-0.91799070	-0.91799075
					$\langle r^{-1} \rangle$	1.6874313	1.6874314
					$\langle r \rangle$	0.92722334	0.92722332
					$\langle r^2 \rangle$	1.1847192	1.1847192
50	9	5.55	1.78	-42258	$E_T$	-2556.4504	-2556.4508
					$\epsilon_{1s}$	-1261.8878	-1261.8882
					$\langle r^{-1} \rangle$	53.3364	53.3366
					$\langle r \rangle$	0.0288512	0.0288521
					$\langle r^2 \rangle$	0.0011245	0.0011243
Be-like systems ( $1s^2 2s^2\ ^1S_0$ )							
4	12	0.76814	1.31884	-156.9	$E_T$	-14.57589220	-14.57589233
					$\epsilon_{1s}$	-4.73349813	-4.73349837
					$\epsilon_{2s}$	-0.30932213	-0.30932218
					$\langle r^{-1} \rangle_{1s}$	3.6833012	3.6833012
					$\langle r^{-1} \rangle_{2s}$	0.5226709	0.5226708
					$\langle r \rangle_{1s}$	0.41489135	0.41489138
					$\langle r \rangle_{2s}$	2.6489444	2.6489432
					$\langle r^2 \rangle_{1s}$	0.23285501	0.23285505
					$\langle r^2 \rangle_{2s}$	8.4236691	8.4236429
					50	20	11.30345
$\epsilon_{1s}$	-1241.39323	-1241.39333					
$\epsilon_{2s}$	-297.934671	-297.934579					
$\langle r^{-1} \rangle_{1s}$	53.311598	53.311611					
$\langle r^{-1} \rangle_{2s}$	13.123591	13.123571					
$\langle r \rangle_{1s}$	0.02886990	0.02886991					
$\langle r \rangle_{2s}$	0.1178252	0.1178255					
$\langle r^2 \rangle_{1s}$	0.00112588	0.00112588					
$\langle r^2 \rangle_{2s}$	0.01632213	0.01632217					

<sup>A</sup>  $E_T$  is the total energy (a.u.);  $\epsilon_i$  is the eigenvalue of orbital  $i$  (a.u.);  $\langle r^n \rangle_i$  is the expectation of  $r^n$  of orbital  $i$ .

At high values of  $Z$ , the Coulomb cusp exponent is difficult to fit with functions of the form  $r^n \exp(-\zeta r)$ , where  $n$  is an integer. Near a point nucleus,  $P(r)$  and  $Q(r)$  are both proportional to  $r^\gamma$ , when  $|\kappa| = 1$ , i.e. for  $s$  and  $p_{1/2}$  electrons  $\gamma < 1$ , so that  $P(r)$  and  $Q(r)$  have infinite derivatives at  $r = 0$  (Grant 1983; pp. 75–6). This means that very large values of  $\zeta$  may be required to simulate the behaviour at the origin,

**Table 2.** Contribution of the Breit operator to the total energy of closed shell atomic ground states for the systems of Table 1 with  $B(R)$  treated as a perturbation and included in the matrix DF SCF

Property	GRASP	$B(R)$ included in matrix DF SCF	
	Perturbative $B(R)$	Perturbative	Self-consistent
$Z = 2, 1s^2 \ ^1S_0$			
$E_B$	$+6.377625 \times 10^{-5}$	$+6.377622 \times 10^{-5}$	
$E_T$	$-2.861813360^A$	$-2.861813340^A$	
$E_B + E_T$	$-2.86174958$	$-2.861749563$	$-2.861749565$
$\epsilon_{1s}$		$-0.91799070$	$-0.91794463$
$\langle r^{-1} \rangle_{1s}$		$1.6874313$	$1.6873746$
$\langle r \rangle_{1s}$		$0.927223$	$0.927255$
$\langle r^2 \rangle_{1s}$		$1.184719$	$1.184800$
$Z = 50, 1s^2 \ ^1S_0$			
$E_B$	$+1.70225482$	$+1.70224876$	
$E_T$	$-2556.4508^A$	$-2556.4504^A$	
$E_B + E_T$	$-2554.7485$	$-2554.74811$	$-2554.74942$
$\epsilon_{1s}$		$-1261.88784$	$-1260.20392$
$\langle r^{-1} \rangle_{1s}$		$53.336$	$53.284$
$\langle r \rangle_{1s}$		$0.028851$	$0.028880$
$\langle r^2 \rangle_{1s}$		$0.0011267$	$0.001124$
$Z = 4, 1s^2 2s^2 \ ^1S_0$			
$E_B$	$+7.0247690 \times 10^{-4}$	$+7.0247690 \times 10^{-4}$	
$E_T$	$-14.57589233^B$	$-14.57589220^B$	
$E_B + E_T$	$-14.5751899$	$-14.575189718$	$-14.575189759$
$\epsilon_{1s}$		$-4.733498$	$-4.732940$
$\epsilon_{2s}$		$-0.309322$	$-0.309309$
$\langle r^{-1} \rangle_{1s}$		$3.683301$	$3.683022$
$\langle r \rangle_{1s}$		$0.414891$	$0.414923$
$\langle r^2 \rangle_{1s}$		$0.232855$	$0.232890$
$\langle r^{-1} \rangle_{2s}$		$0.522671$	$0.522653$
$\langle r \rangle_{2s}$		$2.648944$	$2.649044$
$\langle r^2 \rangle_{2s}$		$8.423669$	$8.424281$
$Z = 50, 1s^2 2s^2 \ ^1S_0$			
$E_B$	$+2.054634$	$+2.054633$	
$E_T$	$-3159.987438^B$	$-3159.987310^B$	
$E_B + E_T$	$-3157.932804$	$-3157.932677$	$-3157.934248$
$\epsilon_{1s}$		$-1241.3932$	$-1239.5639$
$\epsilon_{2s}$		$-297.9347$	$-297.7447$
$\langle r^{-1} \rangle_{1s}$		$53.3116$	$53.2531$
$\langle r \rangle_{1s}$		$0.0288699$	$0.0289014$
$\langle r^2 \rangle_{1s}$		$0.00112588$	$0.00112829$
$\langle r^{-1} \rangle_{2s}$		$13.1236$	$13.1179$
$\langle r \rangle_{2s}$		$0.117825$	$0.117894$
$\langle r^2 \rangle_{2s}$		$0.016322$	$0.016341$

<sup>A</sup> From Table 1 for the He-like system.

<sup>B</sup> From Table 1 for the Be-like system.

causing a violation of (21). We have been able to demonstrate that the method no longer gives variational upper bounds when this is the case, and that one can make eigenvalues descend below the correct values slowly, but monotonically, as  $\zeta$  increases above the critical value. There are two ways to eliminate this problem, which has implications for convergence as  $N$ , the basis set size, increases: the simplest is to use a distributed charge model for the nucleus, and there is some evidence to show that this removes the need to use large  $\zeta$  values (Ishikawa *et al.* 1985). The second way is to include a single function with the correct cusp behaviour along with the rest of the basis set; this has not yet been studied.

**Table 3. Matrix Dirac-Fock energies for HCl**

Large component basis sets: (10s, 6p) GTO from Roos and Siegbahn (1970) for Cl; (7s, 4p) GTO from Schmidt and Ruedenberg (1979) for H; small component basis sets from equation (18). All energies and lengths in atomic units

<i>Experimental bond length (<math>R = 2.4087</math> a.u.)</i>		
Quantity	Value	Method
$E_{\text{nonrel}}$	-459.9810	Present matrix DF, $c \rightarrow \infty$
$E_{\text{nonrel}}$	-460.1103	Hartree-Fock limit (Cade and Huo 1973)
$E_{\text{nonrel}}$	-460.1153	Finite difference Hartree-Fock (Laaksonen <i>et al.</i> 1983c)
$E_{\text{rel}}$	-461.4417	Present matrix DF
$E_{\text{rel}} - E_{\text{nonrel}}$	-1.4607	Present matrix DF

*Variation with bond length*

$R$	Quantity	Rel.	Nonrel.	Diff.
2.35	$E_{\text{T}}$	-461.44127	-459.9807	-1.4606
2.40	$E_{\text{T}}$	-461.44174	-459.9810	-1.4607
2.45	$E_{\text{T}}$	-461.44130	-459.9805	-1.4608
	$R_{\text{eq}}$	2.401	2.396	0.005

We have also done some calculations on simple diatomics by adapting the ATMOL package to compute the extra integrals required (Laaksonen *et al.* 1986). Table 3 gives some results obtained with this code for HCl using a basis with 10s, 6p functions on Cl (Roos and Siegbahn 1970) and 7s, 4p functions on H (Schmidt and Ruedenberg 1979) near the equilibrium separation, experimentally 2.4087 bohr. Clearly, as the nonrelativistic total energy is well above the Hartree-Fock limit, these results can only be taken as preliminary, although it seems as though the predicted relativistic bond length may be marginally closer to the experimental value. The basis set is about as large as can be accommodated on the FPS-164 processor in Tampere, where the calculations were done. Further work is clearly needed on this problem.

We have also investigated two other approaches, both based on the partitioned equation for the large component  $p$  of (20):

$$\{T_{\pi\pi} + V_{\pi\pi} + K(\epsilon)\}p = \epsilon S_{\pi\pi} p, \quad (23)$$

**Table 4.** Numerical finite-difference two-dimensional calculations of low-lying states of diatomic molecules

All energies and lengths are in atomic units unless otherwise specified; radial moments are measured relative to the midpoint of the molecular bond

<i>One-electron systems at <math>R = 2.0</math> a.u.</i>					
System	State	$E_{\text{rel}}$	$E_{\text{nonrel}}$	Diff. ( $\times 10^6$ )	Ref.
$\text{H}_2^+$	$1\sigma_g(1s\sigma_g)$	-1.1026415709	-1.1026342145	-7.3564	A
				-7.36	B
				-7.38	C
				-7.381	D
$\text{HeH}^{2+}$	$3\sigma_u(2p\sigma_u)$	-0.6675527640	-0.6675343923	-1.8372	A
				-1.0308	A

<i>Two-electron systems in their ground states</i>						
System	$R$	Property	Value (rel)	Value (nonrel)	Diff.	
$\text{H}_2$	1.4	$E_T$	-1.13364396 <sup>E</sup>	-1.13362957 <sup>F</sup>	$-1.439 \times 10^{-5}$	
			-1.13364349	-1.13362909 <sup>G</sup>	$-1.44 \times 10^{-5}$	
			-1.129791	-1.129777 <sup>H</sup>	$-1.4 \times 10^{-5}$	
		$\epsilon$	-0.59466236 <sup>E</sup>	-0.59465857 <sup>F</sup>		
			-0.59466232	-0.59465853 <sup>G</sup>		
			-0.59418	-0.59458 <sup>H</sup>		
			$\langle r^2 \rangle$	2.573887 <sup>E</sup>	2.573930 <sup>F</sup>	
$Q_2^e$	0.2432894 <sup>E</sup>	0.2432888 <sup>F</sup>				
$Q_4^e$	0.090721 <sup>E</sup>	0.090721 <sup>E</sup>				
$\text{HeH}^+$	1.455	$E_T$	-2.93323178 <sup>E</sup>	-2.93310325 <sup>F</sup>	$-1.285 \times 10^{-4}$	
			-1.63748755 <sup>E</sup>	-1.63745062 <sup>F</sup>		
			-0.49448234 <sup>E</sup>	-0.49445996 <sup>F</sup>		
		$\epsilon = \langle z \rangle$	$Q_1^e$	0.2432894 <sup>E</sup>	0.2432888 <sup>F</sup>	
			$Q_2^e$	-0.2315366 <sup>E</sup>	-0.2315246 <sup>F</sup>	
			$Q_3^e$	0.090721 <sup>E</sup>	0.090721 <sup>F</sup>	
			$Q_4^e$	0.090721 <sup>E</sup>	0.090721 <sup>F</sup>	
$\langle r^2 \rangle$	2.573887 <sup>E</sup>	2.573930 <sup>F</sup>				
$\text{He}$		$E_T$	-2.861813 <sup>E</sup>	-2.861679996 <sup>F</sup>		
			-2.86181336 <sup>I</sup>			
		$\epsilon$	-0.9179907 <sup>E</sup>			
			-0.91799075 <sup>I</sup>			
		$\langle r \rangle$	0.927223 <sup>E</sup>			
			0.927223 <sup>I</sup>			
$\langle r^2 \rangle$	1.1847193 <sup>E</sup>					
	1.1847192 <sup>I</sup>					

<sup>A</sup> Laaksonen and Grant (1984 *a*). Numerical integration of two-centre Dirac equation in elliptic coordinates  $\xi = (r_1 + r_2)/R$ ,  $\eta = (r_1 - r_2)/R$  transformed to  $\xi = \cosh \mu$ ,  $\eta = \cos \nu$  using a mesh with 193 points in  $\mu$  and 97 points in  $\nu$ .

<sup>B</sup> Mark and Schwarz (1982).

<sup>C</sup> Luke *et al.* (1969).

<sup>D</sup> Bishop (1977).

<sup>E</sup> Laaksonen and Grant (1984 *b*).

<sup>F</sup> Laaksonen *et al.* (1983 *b*).

<sup>G</sup> F. Mark and W. H. E. Schwarz (personal communication).

<sup>H</sup> Matsuoka *et al.* (1980).

<sup>I</sup> Equivalent data from 1-D numerical calculation with GRASP (Dyall *et al.* 1986).

where

$$K(\epsilon) = -\frac{1}{2}(\mathbf{II}_\kappa)_{\pi\rho} S_{\rho\rho}^{-1}(\epsilon S_{\rho\rho} - V_{\rho\rho})\{(\epsilon + 2c^2)S_{\rho\rho} - V_{\rho\rho}\}^{-1}\{(\mathbf{II}_\kappa)_{\pi\rho}\}^\dagger.$$

Wood *et al.* (1985) studied this equation as a way of overcoming the basis set problems described by Dyall *et al.* (1984*a*). Although  $K(\epsilon)$  is a rational function of  $\epsilon$ , Wood *et al.* showed that iterative solution for the eigenvalue is very straightforward, and that the method gives useful results in the hydrogenic case. Laaksonen and Grant (1984*a*, 1984*b*) used the correspondingly partitioned differential equation to solve the DF problem for the ground states of  $\text{H}_2^+$ ,  $\text{HeH}^{2+}$ ,  $\text{H}_2$  and  $\text{HeH}^+$ . The two-dimensional finite-difference numerical method for solving the differential equation had previously been applied to a number of nonrelativistic molecular problems by Laaksonen *et al.* (1983*a-c*). The results of Laaksonen and Grant (1984*a*, 1984*b*) appear in Table 4.

## 5. Conclusions

Evidence continues to accumulate to support the view that methods of calculation of atomic structure as implemented in the GRASP package have a secure theoretical foundation. At the same time, there remain a number of important problems to solve which will need to be tackled if, for example, we are to treat molecules containing heavy atoms with confidence. Some of the practical issues involving basis sets have been resolved, as shown in the last section; whilst much remains to be done to establish good basis sets for heavy atoms, the lines of development are now clearly established. We argued in Section 2 that the SCF methods should be seen in the context of a perturbation theory model. Some headway has been made by calculating radial correlation energies using matrix DF wavefunctions (Quiney *et al.* 1986) but much more remains to be done.

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## References

- Barrett, R. C., and Jackson, D. F. (1977). 'Nuclear Sizes and Structure' (Clarendon: Oxford).  
 Berrington, K. A., Burke, P. G., LeDourneuf, M., Robb, W. D., Taylor, K. T., and Vo Ky Lan (1978). *Comput. Phys. Commun.* **14**, 367.  
 Bishop, D. M. (1977). *J. Chem. Phys.* **66**, 3842.  
 Björken, J. D., and Drell, S. D. (1954). 'Relativistic Quantum Mechanics' (McGraw-Hill: New York).  
 Breit, G. E. (1930). *Phys. Rev.* **36**, 383.  
 Breit, G. E. (1932). *Phys. Rev.* **39**, 616.

- Burke, P. G., and Robb, W. D. (1975). In 'Advances in Atomic and Molecular Physics', Vol. 11 (Eds D. R. Bates and B. Bederson), pp. 143-214 (Academic: New York).
- Cade, P. E., and Huo, W. (1973). *At. Data Nucl. Data Tables* **13**, 415.
- Chang, J. J. (1975). *J. Phys. B* **8**, 2327.
- Chang, J. J. (1977). *J. Phys. B* **10**, 3335.
- Condon, E. U., and Shortley, G. M. (1951). 'Theory of Atomic Spectra' (Cambridge Univ. Press).
- Desclaux, J. P. (1975). *Comput. Phys. Commun.* **9**, 31.
- Dietz, K., Lechtenfeld, O., and Weymans, G. (1982). *J. Phys. B* **15**, 4301, 4315.
- Dirac, P. A. M. (1930). *Proc. R. Soc. London A* **126**, 360.
- Drake, G. W. F., and Goldman, S. P. (1981). *Phys. Rev. A* **23**, 2093.
- Dyall, K. G. (1986). *Aust. J. Phys.* **39**, 667.
- Dyall, K. G., Grant, I. P., and Plummer, E. P. (1986). *Comput. Phys. Commun.* (in preparation).
- Dyall, K. G., Grant, I. P., and Wilson, S. (1984a). *J. Phys. B* **17**, 493.
- Dyall, K. G., Grant, I. P., and Wilson, S. (1984b). *J. Phys. B* **17**, L45.
- Dyall, K. G., Grant, I. P., and Wilson, S. (1984c). *J. Phys. B* **17**, 1201.
- Furry, W. H. (1951). *Phys. Rev.* **81**, 115.
- Gell-Mann, M., and Low, F. E. (1951). *Phys. Rev.* **84**, 350.
- Grant, I. P. (1970). *Adv. Phys.* **19**, 747.
- Grant, I. P. (1982). *Phys. Rev. A* **25**, 1220.
- Grant, I. P. (1983). In 'Relativistic Effects in Atoms, Molecules and Solids' (Ed. G. L. Malli), pp. 55-114 (Plenum: New York).
- Grant, I. P., McKenzie, B. J., Norrington, P. H., Mayers, D. F., and Pyper, N. C. (1980). *Comput. Phys. Commun.* **21**, 207.
- Grotch, H., and Yennie, D. R. (1969). *Rev. Mod. Phys.* **41**, 350.
- Hylleraas, E. A., and Undheim, B. (1930). *Z. Phys.* **65**, 759.
- Ishikawa, Y., Baretty, R., and Binning, R. C. (1985). *Chem. Phys. Lett.* **121**, 130.
- Johnson, C., and Grant, I. P. (1986). (in preparation).
- Kagawa, T. (1975). *Phys. Rev. A* **12**, 2245.
- Kagawa, T. (1980). *Phys. Rev. A* **22**, 2340.
- Kim, Y.-K. (1967). *Phys. Rev.* **154**, 17; **159**, 190(E).
- Klapisch, M., Schwob, J. L., Fraenkel, B. S., and Oreg, J. (1977). *J. Opt. Soc. Am.* **67**, 148.
- Kutzelnigg, W. (1984). *Int. J. Quantum Chem.* **25**, 107.
- Laaksonen, L., and Grant, I. P. (1984a). *Chem. Phys. Lett.* **109**, 485.
- Laaksonen, L., and Grant, I. P. (1984b). *Chem. Phys. Lett.* **112**, 157.
- Laaksonen, L., Grant, I. P., and Wilson, S. (1986). (in preparation).
- Laaksonen, L., Pyykkö, P., and Sundholm, D. (1983a). *Int. J. Quantum Chem.* **23**, 309.
- Laaksonen, L., Pyykkö, P., and Sundholm, D. (1983b). *Int. J. Quantum Chem.* **23**, 319.
- Laaksonen, L., Pyykkö, P., and Sundholm, D. (1983c). *Chem. Phys. Lett.* **96**, 1.
- Luc-Koenig, E. (1972). *Physica* **62**, 393.
- Luc-Koenig, E. (1976). *Phys. Rev. A* **13**, 2114.
- Luke, S. K., Hunter, G., McEachran, R. P., and Cohen, M. (1969). *J. Chem. Phys.* **50**, 1644.
- MacDonald, J. K. L. (1933). *Phys. Rev.* **43**, 830.
- McKenzie, B. J., Grant, I. P., and Norrington, P. H. (1980). *Comput. Phys. Commun.* **21**, 233.
- Mark, F., and Schwarz, W. H. E. (1982). *Phys. Rev. Lett.* **48**, 673.
- Matsuoka, O., Suzuki, N., Aoyama, T., and Malli, G. (1980). *J. Chem. Phys.* **73**, 1320.
- Mohr, P. J. (1974). *Ann. Phys. (New York)* **88**, 26, 52.
- Mohr, P. J. (1975). *Phys. Rev. Lett.* **34**, 1050.
- Mohr, P. J. (1982). *Phys. Rev. A* **26**, 2338.
- Norrington, P. H., and Grant, I. P. (1981). *J. Phys. B* **14**, L261.
- Norrington, P. H., and Grant, I. P. (1985). Contributed Paper H40, 14th Int. Conf. on the Physics of Electronic and Atomic Collisions, Palo Alto, California.
- Quiney, H. M., Grant, I. P., and Wilson, S. (1986). *J. Phys. B* (in press).
- Roos, B., and Siegbahn, P. (1970). *Theor. Chim. Acta* **17**, 209.
- Safronova, U. I., and Rudzikas, Z. B. (1976). *J. Phys. B* **9**, 1989.
- Salpeter, E. E., and Bethe, H. A. (1951). *Phys. Rev.* **84**, 1232.
- Schmidt, M. W., and Ruedenberg, K. (1979). *J. Chem. Phys.* **71**, 3951.

- Scott, N. S., and Burke, P. G. (1980). *J. Phys. B* **13**, 4299.
- Scott, N. S., and Taylor, K. T. (1982). *Comput. Phys. Commun.* **25**, 347.
- Sucher, J. (1980). *Phys. Rev. A* **22**, 348.
- Wilkinson, J. H. (1965). 'The Algebraic Eigenvalue Problem' (Clarendon: Oxford).
- Wood, J., Grant, I. P., and Wilson, S. (1985). *J. Phys. B* **18**, 3027.

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