



Chapter 2.15

Keywords: relativistic wavefunctions; Hartree–Fock; Dirac–Fock; configuration interaction; angular momentum coupling; transition energies; transition rates; oscillator strengths.

Relativistic effects on energies, transitions and basis states

Alan Hibbert*

School of Mathematics and Physics, Queen's University of Belfast, Belfast BT7 1NN, United Kingdom. *Correspondence e-mail: a.hibbert@qub.ac.uk

Some of the methods used to determine wavefunctions for atoms and ions, using both nonrelativistic and relativistic formulations, are reviewed, focusing on the use of the generic configuration interaction approach for many-electron systems. Some examples of the importance of relativistic effects for transition energies and transition rates are shown.

1. Introduction

The quantum-mechanical calculation of atomic properties commenced with the introduction of the nonrelativistic Schrödinger equation (Schrödinger, 1926),

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t}, \quad (1)$$

and for stationary-state (time-independent) solutions,

$$\Psi = \psi(\mathbf{r}) \exp(-iEt/\hbar), \quad (2)$$

where ψ is independent of time, so that the spatial wavefunction ψ is an eigenfunction of the Hamiltonian,

$$H\psi = E\psi. \quad (3)$$

Applications developed quickly over the following few years. At first, wavefunctions and energies of hydrogen-like ions were determined: they could be obtained in a closed and exact form. Explicitly, it is possible to separate the radial and angular coordinate dependence as

$$\psi(\mathbf{r}) = \frac{1}{r} P_{nl}(r) Y_l^m(\theta, \varphi) \quad (4)$$

and the energy E depends only on the integer n . The spherical harmonic Y_l^m is also an eigenfunction of the angular momentum operators \mathbf{L}^2 and L_z , with eigenvalues $\hbar^2 l(l+1)$ and $\hbar m$, respectively. These two operators commute with the Hamiltonian. However, the components of \mathbf{L} do not commute with each other; instead,

$$[L_x, L_y] = i\hbar L_z. \quad (5)$$

Similarly, wavefunctions for the hydrogen molecular ion H_2^+ could be obtained analytically (see, for example, Bransden & Joachain, 1983). However, when attention turned to atoms and molecules with more than one free electron, it was no longer possible to obtain exact wavefunctions because the electron–electron interaction potential prevented a separation-of-variables approach to the solution of Schrödinger's equation. Good approximate solutions were quickly determined for systems with two electrons [for example, by the work of Hylleraas (1929) in the case of the two-electron neutral helium] and by Hartree (1928*a,b*), with the method augmented

Related chapters

Volume I: 2.1, 2.2, 2.7, 2.8, 2.13, 8.17

by Fock (1930) or Slater (1930) for atoms with more than two electrons.

These nonrelativistic methods did not treat electron spin adequately, and it was Dirac who introduced this concept properly through his relativistic treatment of one-electron systems (Dirac, 1928*a,b*), which was subsequently extended to many-electron systems through methods similar to those of Hartree.

Apart from the few atomic and molecular systems for which exact solutions could be obtained, only approximate wavefunctions could be determined during these early years. For two-electron (helium-like) atomic systems, some key features of these approximate solutions could be discerned from the calculations. Hartree and, at times, his father (see, for example, Hartree & Hartree, 1936) did undertake very careful and intricate calculations for many-electron systems, based on the theory that he and Fock developed. However, more accurate solutions did not become possible until the 1950s, when the development of electronic computers took the drudgery out of the calculations.

2. Nonrelativistic wavefunctions

The calculation of any atomic property requires knowledge of the wavefunctions of the relevant atomic states. If we neglect the effects of relativity, these wavefunctions Ψ_n are solutions of Schrödinger's equation,

$$H\psi_n = i\hbar \frac{\partial \psi_n}{\partial t}. \quad (6)$$

The Hamiltonian H consists of the total kinetic energy of the N electrons plus the total potential energy of the electrons due to their electrostatic interactions with the nucleus and with each other,

$$H = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j} \frac{1}{r_{ij}}, \quad (7)$$

where we have used atomic units (au), for which \hbar and the electronic charge (e) and the reduced mass (μ) of the electron are all set equal to unity; $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and the nucleus is taken as the origin of coordinates; Z is the nuclear charge.

The terms in the single summations are simply sums of hydrogenic Hamiltonians. If the final term (double sum) were absent, the Hamiltonian would be capable of exact solutions. The double sum, involving the coordinates of two electrons, precludes the determination of wavefunctions exactly, so that approximate methods, usually based on perturbation or (more often) variational theory, must be used.

2.1. Angular momentum

The angular momentum operators of the individual electrons no longer commute with the Hamiltonian because of the inter-electronic potential. However, if we construct a total (orbital) angular momentum operator

$$\mathbf{L} = \sum_{i=1}^N \mathbf{L}_i, \quad (8)$$

then \mathbf{L}^2 and L_z [with eigenvalues $L(L+1)$ and $M_L = \sum_i M_{L_i}$] do commute with the Hamiltonian, so that the wavefunction can be characterized by these eigenvalues as well as the associated energy. The individual spins of the electrons couple in the same manner to form spin angular momentum operators \mathbf{S}^2 and S_z with eigenvectors $S(S+1)$ and $M_S = \sum_i M_{S_i}$. As the Hamiltonian does not involve spin functions, these operators necessarily commute with the Hamiltonian. Thus, the wavefunction is characterized as $\psi(LSM_LM_S)$ and this coupling scheme is usually known as LS coupling. It is often assumed that the orbital and spin angular momenta can be coupled independently. In the case of a configuration such as $1s^2 2s^2 2p 3p$ this is true: the possible symmetries (arising from the *inequivalent* $2p$ and $3p$ orbitals) are 1S , 3S , 1P , 3P , 1D and 3D . However, for two *equivalent* p orbitals, as in the configuration $1s^2 2s^2 2p^2$, then only 1S , 3P and 1D are possible.

2.2. The Hartree–Fock (HF) method

The most common starting point for many-electron systems is the HF method. Originally, Hartree proposed that the wavefunction be written as a product of functions, with each being a function of the coordinates of a single electron. These functions were to be determined as the solution of a Schrödinger-type equation with a potential comprising the electron–nucleus interaction and the spherical average of the interaction between each electron and the charge cloud of all the other electrons.

However, such a wavefunction does not satisfy the requirement of being antisymmetric with respect to the interchange of the coordinates of any pair of electrons. This problem was overcome by Fock (1930), who expressed the wavefunction as an *antisymmetrized* product of one-electron functions, in the form of one or more (to ensure that the wavefunction is an eigenfunction of the angular momentum operators) determinants of the one-electron functions – orbitals – or more correctly spin-orbitals since they are expressed as the product of a spatial function $u_i(\mathbf{r})$ and a spin function, with $m_s = \frac{1}{2}$ or $m_s = -\frac{1}{2}$. The application of the variational principle gives rise to the HF equations. Usually, the spatial function is represented by a product of a radial function and a single spherical harmonic, which is the same form as the wavefunctions for a one-electron ion; even though the radial functions will differ from their hydrogenic counterparts, the angular dependence as a spherical harmonic will be the same. This choice reduces the number of HF equations, since the radial functions depend only on n and l , and not on the m values.

Two difficulties immediately arise.

- (i) These HF equations are nonlinear in u_i .
- (ii) The potential in each equation is nonlocal, in the sense that it does not appear in the equation as a function simply to be multiplied by u_i .

As a consequence, the equations have to be solved iteratively until self-consistency is achieved. Two approaches have been used by many authors. One approach is to solve the HF equations numerically (Hartree, 1957; Froese Fischer, 1977).

Table 1
Ground-state energy (au) of helium (Bunge, 1970).

<i>s</i> -limit	−2.87903
+ <i>p</i> -limit	−2.90051
+ <i>d</i> -limit	−2.90275
+ <i>f</i> -limit	−2.90331
+ <i>g</i> -limit	−2.90347
⋮	⋮
Exact (nonrelativistic)	−2.90372

In the other approach, the radial functions are written as sums of analytic basis functions, usually Slater-type orbitals (STOs) for atomic systems; the parameters of the STOs are treated as variational parameters, and for each choice of such parameters the HF equations reduce to nonlinear coupled algebraic equations for the coefficients of the STOs in each radial function (Roothaan, 1951; Clementi & Roetti, 1974).

2.3. Configuration interaction

The HF method, while forming a good foundation for atomic structure calculations, is still an approximation. It is customary to refer to the difference

$$E^{\text{corr}} = E^{\text{exact}} - E^{\text{HF}} \quad (9)$$

as the *correlation energy*, and to methods of capturing some or ideally all of the correlation energy as correlation effects. The HF method does include some degree of dealing with the correlation of the motion of the electrons. However, it presupposes that the atomic state can be described by a single configuration and that the orbital functions can be represented by a single product of a spatial function and a spin function, with the spatial function itself represented by a product of a radial function and a single spherical harmonic. Thus, the ground state of two-electron ions would be represented by the configuration $1s^2 \ ^1S$, while the lowest odd-parity singlet state would be $1s2p \ ^1P^o$. The $1s$ orbital implies a spherical harmonic Y_0^0 and $2p$ implies Y_1^m with $m = 0, \pm 1$. However, as we have noted, the individual angular momentum operators of the electrons do not commute with the Hamiltonian; only the *total* angular momenta L and S are good quantum numbers. Other configurations can also result in a total symmetry of 1S , for example $2p^2, 3d4d, \dots$. Similarly, for the $1s2p \ ^1P^o$ state one might also include configurations such as $nsmp, npmd \dots$. If we describe each of these configurations by a configuration state function (CSF) $\psi_i(LS)$ then a more general form of the wavefunction incorporating these ideas would be

$$\psi(LS) = \sum_{i=1}^M a_i \Phi_i(LS). \quad (10)$$

This is the form of wavefunction for a number of methods under the ‘umbrella’ title of configuration interaction (CI).

The angular and spin functions in configuration interaction wavefunctions are defined by the *nl* of the orbitals in the CSFs, with a well defined coupling scheme of the angular momenta of the electrons to give a total L and S . There remain two quantities which are yet to be determined: the radial functions and the *mixing* or CI coefficients a_i .

If we choose a set of radial functions then the CSFs are fixed. Applying the variational principle to the CI wavefunction, in which we minimize $\langle \psi | H | \psi \rangle$ subject to $\langle \psi | \psi \rangle = 1$, we obtain

$$\sum_{j=1}^M (H_{ij} - E\delta_{ij})a_j = 0, \quad (11)$$

with the Hamiltonian matrix defined by $H_{ij} = \langle \Phi_i | H | \Phi_j \rangle$. Hence, the Lagrange multiplier E is an eigenvalue of the Hamiltonian matrix and the CI coefficients are the components of the corresponding eigenvector.

There will be M such eigenvalues and eigenvectors. The Hylleraas–Undheim theorem (or, equivalently, the Cauchy interlacing theorem; Hylleraas & Undheim, 1930; MacDonald, 1933) ensures that if the eigenvalues E_i are ordered so that $E_i < E_{i+1}$, then

$$E_i > E_i^{\text{exact}}, \quad (12)$$

where by ‘exact’ we mean the lowest possible eigenvalue within the approximations of the model, in this case LS symmetry and parity π . This inequality provides a set of variational principles for *each* of the eigenvalues. Thus, given that the eigenvalues correspond to the energies of the various states of a specific $LS\pi$, we may use any of the eigenvalues as a function to be minimized as we optimize the radial functions of the orbitals. Moreover, if (as is often the case) we wish to determine wavefunctions for numerous states simultaneously, we can optimize different orbitals on different eigenvalues. This makes for a balanced treatment of these states, ensuring that we do not find a few states to be well represented while others are poorly represented. The underlying process is to vary the radial functions and, for any particular set of radial functions, to obtain the energy eigenvalues by diagonalizing the corresponding Hamiltonian matrix, finishing when no further lowering of the eigenvalue of choice is achievable.

Within the genre of configuration interaction, there are several methods in widespread use, mostly distinguished by their different approaches to the determination or representation of the radial functions. In the multi-configurational Hartree–Fock (MCHF) procedure (Froese Fischer, 1970, 1978, 1991; Froese Fischer, Brage *et al.*, 1997; Froese Fischer, Gaigalas *et al.*, 1997) the variational principle is used, in the same manner as for the HF equations, to derive coupled integro-differential equations which are solved numerically and iteratively until self-consistency is reached, with the added requirement that at each iteration the Hamiltonian matrix is diagonalized to determine the CI coefficients. The CIV3 code (Hibbert, 1975) undertakes a parallel process with analytic basis functions (sums of STOs) representing the radial functions of the orbitals. Usually, the energies obtained are slightly lower with the MCHF method because it is not constrained by the limited number of basis functions used in CIV3. Other processes such as those adopted in *SUPERSTRUCTURE* (Eissner *et al.*, 1974) or *AUTOSTRUCTURE* (Badnell, 1986) calculate the radial functions as eigenfunctions of one-electron Schrödinger-type equations with potentials that are variously

Table 2
 2D state energies (cm^{-1}) of Si II.

$$E_1 = E(3s^23p^2P^o), E_2 = E(3s3p^2^2D), E_3 = E(3s^23d^2D).$$

Calculation	$E_2 - E_1$	$E_3 - E_2$
A	53955	25302
B	53994	25037
C	54323	24846
D	54567	24736
E	54881	24405
F	55254	24149
Experimental	55127	24030

predetermined, for example using a scaled Thomas–Fermi approach. Again, some codes use model potentials with adjustable parameters chosen to produce accurate energy eigenvalues. Within such models, however, accurate energies do not necessarily imply accurate wavefunctions.

In general, the CI expansion is slowly converging with respect to the l values of the orbitals introduced in the expansion, and to a lesser extent with respect to the n values. In Table 1 we give a simple illustrative example for the ground state of helium as calculated by Bunge (1970). Clearly, an extrapolation of these results would indicate that much higher l values would be required to achieve convergence.

The difficulty is magnified when more than one atomic state needs to be discussed simultaneously. While the variational principle ensures that the energy of each state is lowered as more configurations are included in the calculation (an increase in M), there is no guarantee that the difference in energy between the two states converges monotonically to the experimental value. There is no variational principle for energy differences. Unfortunately, it is often the accuracy to which the difference in energy between two or more states is calculated that determines the overall accuracy of the CI expansion of the wavefunctions, and therefore the accuracy of other atomic properties which use these wavefunctions.

As an example of this difficulty, let us consider the two lowest 2D states of Si II, written as $3s3p^2$ and $3s^23d$. Hibbert *et al.* (1992) undertook a systematic sequence of calculations (A–F) as shown in Table 2. The energies E_1 , E_2 and E_3 are those of $3s^23p^2^2P^o$, $3s3p^2^2D$ and $3s^23d^2D$, respectively. Calculation A contained some basic configurations of both $^2P^o$ and 2D symmetries, while calculation F involved many more configurations. The experimental energy differences are from Martin & Zalubas (1983). It can be seen that both energy separations converge slowly. In this particular example, the key difference is that between the two 2D states. The transition rate from $3s3p^2^2D$ to the ground state is very sensitive to the accuracy of the calculation of this energy difference, and it is this transition rate which influences the determination of the abundance of Si II in the interstellar medium.

Inaccuracies in the mixing coefficients a_i in equation (10) are a consequence of inaccuracies in the energy separation of two or more strongly interacting states and this leads to, in this case, substantial inaccuracies in the rates of transitions to the ground level. A number of extrapolation processes have been developed to try to rectify these errors. One such process is adopted in the use of the Cowan code (Cowan, 1981). This

code was written with one of its principal aims being to enable experimentalists to use spectroscopic data in the determination of energy levels. Often, a relatively simple CI model is built and the two-electron radial integrals (Slater integrals) can be treated as adjustable parameters optimized to fit known experimental data. The consequence is a reduction in the value of the Slater integrals from their *ab initio* values by factors in the region of 0.80–0.85. These are then used to determine good approximations to the energies of other levels. This has proved to be a very successful process. However, as the assumed CI expansions are often rather short and also assume that an orbital function is the same in all configurations in which it appears (which is generally not the case), some caution has to be noted in using mixing coefficients obtained by this method.

A different approach is provided by the ‘fine-tuning’ process that has frequently been adopted (Nicolaidis & Beck, 1975; Hibbert, 1996) whereby small adjustments are made to some diagonal elements of the Hamiltonian matrix to bring the calculated energy eigenvalue differences into closer agreement with experiment. Both of these processes normally *improve* the accuracy of the mixing coefficients, but they do not ensure complete accuracy.

3. Relativistic wavefunctions

No matter how converged the CI expansions in LS coupling may appear, they fail to reproduce the fine-structure splitting of the LS states. For example, the ground state of the C atom is normally expressed as $1s^22s^22p^2^3P$. However, in reality this ‘state’ is split into three distinct levels separated by 16.4 and 27.0 cm^{-1} . Schrödinger’s equation does not predict this fine-structure splitting. To do so, it is necessary to use a relativistic approach to the construction of wavefunctions. A comprehensive account of the form, construction and use of relativistic wavefunctions is provided by Grant (2007). Here, we simply outline the key steps.

The theoretical approach in which fine structure appears naturally is based on the use of the Dirac equation (Dirac, 1928*a,b*). The Hamiltonian for a one-electron system takes the form

$$H_D = -\frac{Ze}{r} + \beta E_0 + \alpha \cdot (\mathbf{cp}), \quad (13)$$

where c is the speed of light, while E_0 and \mathbf{p} are the rest-mass energy and momentum of the electron, respectively:

$$E_0 = mc^2, \quad \mathbf{p} = -i\hbar \text{grad}. \quad (14)$$

α and β are 4×4 matrices,

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \quad (15)$$

where I is the 2×2 unit matrix and σ are the 2×2 Pauli spin matrices. As in the nonrelativistic case, the Dirac equation for a one-electron ion can be solved exactly (see, for example, Bethe & Salpeter, 1957; Grant, 2007).

The wavefunction is a vector with four components $(u_1, u_2, u_3, u_4)^T$, referred to as a spinor, the spin of the electron being directly related to the Pauli spin matrices,

$$\mathbf{s} = \frac{1}{2}\hbar\boldsymbol{\sigma}. \quad (16)$$

Thus, the spin of the electron arises naturally. The orbital angular momentum no longer commutes with this Hamiltonian. Instead, the total angular momentum, which is the sum of the orbital and spin angular momenta, does commute with H ,

$$\mathbf{j} = \mathbf{l} + \mathbf{s}. \quad (17)$$

The commuting operators are therefore H, \mathbf{j}^2 with eigenvalues $\hbar^2 j(j+1)$, and one of the components of \mathbf{j} , usually j_z with eigenvalue $\hbar m_j$, and $|l-s| \leq j \leq (l+s)$, so that $j = l \pm \frac{1}{2}$ except that if $l = 0, j = \frac{1}{2}$ only. The wavefunctions depend explicitly on the value of j , so that the hydrogenic orbitals are expressed as $1s_{1/2}, 2p_{1/2}, 2p_{3/2}$ etc. Although the wavefunction contains four components, only two distinct radial functions are involved, $P(r)$ and $Q(r)$, which are referred to as the large and small components on account of their relative amplitudes. When the angular and spin integrals are carried out, there remains a pair of coupled differential equations for P and Q .

3.1. Many-electron systems

The calculation of relativistic wavefunctions for many-electron systems suffers from the same difficulty as for nonrelativistic wavefunctions: the inter-electronic potential renders the equations not open to an exact treatment. The Hartree–Fock (or single-configuration) method is replaced by the Dirac–Fock (DF) method, based on a Hamiltonian of the form (Grant, 2007)

$$H = \sum_{i=1}^N H_D(i) + \sum_{i<j} \left[\frac{1}{r_{ij}} + g^B(r_{ij}) \right], \quad (18)$$

where $g^B(r_{ij})$ is the Breit interaction arising from a quantum electrodynamic treatment of the electron–electron interaction and retaining only the leading terms in the long-wavelength limit,

$$g^B(r_{ij}) = \frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{2r_{ij}} - \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})}{2r_{ij}^3}. \quad (19)$$

The DF equations normally omit the Breit interaction, treating it as a perturbation once the solutions of the DF equations have been obtained. The process for solving the DF equations is similar to that for the HF equations, except that for each orbital the two radial functions P and Q must be obtained, rather than one.

A similar parallel with the nonrelativistic case occurs for multi-configurational wavefunctions. Because of this similarity, the multi-configurational Dirac–Fock (MCDF) method (Desclaux, 1975) is perhaps more properly termed the multi-configurational Dirac–Hartree–Fock (MCDHF) method and is the basis of the *GRASP* suite of computer codes (Grant *et al.*, 1980; Dyllal *et al.*, 1989; Parpia *et al.*, 1996). The angular

momentum operators which commute with the Dirac-based Hamiltonians are those of the total angular momentum: \mathbf{j} for a single electron and $\mathbf{J} = \sum_{i=1}^N \mathbf{j}_i$ for an N -electron system (j – j coupling). A range of additional many-body effects have been introduced and calculated by Indelicato *et al.* (1998), while a new version of *GRASP* permitting the study of lanthanides and actinides has been developed by Jönsson *et al.* (2013).

A number of further investigations have been carried out related to how electrostatic effects should be treated relativistically and how quantum electrodynamic (QED) effects are best represented. For example, Chantler *et al.* (2014) added to the ongoing discussion of whether the Breit interaction should really be included in the self-consistent field optimization of the radial functions of the orbitals or should alternatively continue to be treated perturbatively. They conclude that there is little to be gained by adopting the former, more time-consuming procedure. Lowe *et al.* (2013) proposed a modification to the evaluation of the electron self-energy, based on the model of Welton (1948), in which the interaction between an electron and the electromagnetic field perturbs the motion of the electron, causing it to occupy a somewhat larger region of space than would otherwise be the case. Excellent agreement with other approaches is then obtained.

4. The Breit–Pauli approximation

Calculations based on the Dirac equation incorporate electron spin directly and therefore the observed fine structure of the energy spectrum is described in a natural way, with both wavefunctions and energies being J -dependent. The presence of both large and small components in the orbital radial functions make for a more complicated or extensive calculation when compared with the nonrelativistic approximation. For many heavier atomic systems this fully relativistic procedure is necessary, but for some light or medium atoms and ions a simplification can be made which reduces the number of radial functions to the level expected in a nonrelativistic calculation, effectively by writing the wave equation in terms of a modified Schrödinger-style Hamiltonian.

If the (first-order coupled) Dirac differential equations for the small and large components of the 4-spinor wavefunctions are used to eliminate the small component, giving rise to a set of second-order differential equations for the large components of each of the orbitals, which are then expanded in powers of (v^2/c^2) , a Schrödinger-type equation is obtained. The Hamiltonian comprises the nonrelativistic Hamiltonian together with a number of additional terms: the (nuclear) spin–orbit, the spin–other–orbit, the spin–spin, the orbit–orbit, the Darwin, the mass-correction (or mass–velocity) and the spin–spin contact terms. Of these, the first three cause a splitting of the LS energies into J -dependent levels (hence the fine structure), while the others only modify the overall magnitude of the LS energy. This Breit–Pauli approximation (discussed in detail by Bethe & Salpeter, 1957) in many cases gives a good representation of the energy spectrum.

Within the Breit–Pauli approximation, the *LSJ* or intermediate coupling scheme is used, for which the total **L** and **S** are first determined as in *LS* coupling and the total angular momentum is then $\mathbf{J} = \mathbf{L} + \mathbf{S}$.

The wavefunction can again be written in CI form, but now CSFs with different *L* and *S* can couple together to a common value of *J*,

$$\psi(J) = \sum_{i=1}^M a_i \Phi_i(L_i S_i J). \quad (20)$$

Cowan & Griffin (1976) found that by retaining the mass-correction and Darwin terms in the Hamiltonian during the optimization calculation of the radial functions, a good approximation to the relativistic contraction of the radii of the outer electrons could be obtained for heavy ions. This forms the basis of the *HFR* code (Cowan, 1981). A similar conclusion was reached by Mohan & Hibbert (1987) for the *6s* and *6p* orbitals of neutral mercury using a version of *CIV3* modified along the same lines (Hibbert *et al.*, 1991).

5. Applications

The methods outlined above have been used in many calculations of atomic properties. Since the experimental energy levels are *J*-dependent, it is necessary to incorporate relativistic effects if there is to be genuine comparison between theory and experiment. Here, we simply mention a few applications which illustrate the use of atomic structure calculations and show where relativistic effects arise and the issues encountered in the process.

5.1. Energies

We have already seen in the examples presented in Tables 1 and 2 that the CI expansions can be rather slowly convergent. Tables 1 and 2 show results obtained in *LS* coupling to illustrate the importance of correlation effects, which are principally nonrelativistic in nature. As a consequence, except for systems with very few electrons, experimental accuracy cannot realistically be reached by calculation. Moreover, experimental energies of (or rather, energy differences between) levels are not always available and even approximate energies obtained by calculation are important in the determination of other atomic properties, as we discuss in the following subsection.

However, a *J*-dependent study of energy levels was essential in the particularly complicated situation of levels of Ni II, as was shown by Cassidy *et al.* (2016), in the context of the Breit–Pauli approximation. Up to 60 levels with a common *J* value needed to be described in the same calculation, and for which some of the energies were not known experimentally. Some of the wavefunctions for these levels involved very strong CI mixing. Such mixing is then sensitive to the accuracy of the calculated energy levels, and this directly affects the accuracy with which other properties such as transition rates can be obtained. Comparison of the calculated energies with known

Table 3
CI mixing of $3d^9 4s^2 4p$ *J* = 1 levels in W XLV.

Level	Percentage compositions					
	3D_1	3P_1	1P_1	$(\frac{3}{2}, \frac{1}{2})$	$(\frac{5}{2}, \frac{3}{2})$	$(\frac{3}{2}, \frac{3}{2})$
1	50	22	28	99.3	0.6	0.1
2	5	31	64	0.6	99.0	0.4
3	45	47	8	0.1	0.4	99.5

experimental values enabled us to refine the energies of levels for which no experimental values were available.

So far, we have noted only two choices of angular momentum coupling schemes, *j–j* and *LSJ*, but there are others which are more appropriate for certain systems, such as, for example, the *jK* or *j_cl* scheme appropriate for the $2p^5 nl$ levels of neon-like systems. The choice of angular momentum coupling scheme adopted can have an important effect on the stability of the CI mixing as further CSFs are added and hence on their use in subsequent calculations. For example, in studying the highly ionized tungsten ion W XLV, Spencer *et al.* (2014) found that the $3d^9 4s^2 4p$ levels 3D_1 , 3P_1 and 1P_1 were heavily mixed in *LSJ* coupling, whereas in *j–j* coupling, with the equivalent labelling $(\frac{3}{2}, \frac{1}{2})$, $(\frac{5}{2}, \frac{3}{2})$ and $(\frac{3}{2}, \frac{3}{2})$, the levels are almost pure, as we show in Table 3. All of the coupling schemes are related to each other via unitary transformations. The advantage of choosing the scheme which gives the greatest degree of purity is that when the associated wavefunctions are used for the calculation of other properties, the danger of cancellation due to mixing is reduced to a minimum and this can improve the accuracy of the calculation of these properties.

The relativistic contraction of the radial orbital functions, particularly in *s* electrons, which have a nonzero charge density at the nucleus and are therefore influenced much more by relativity than are electrons with *l* > 0, causes a noticeable shift in mean radii compared with nonrelativistic values, and hence in the transition energies in atomic systems. One consequence is the apparent colour of gold compared with other elements such as silver. When white light shines on metals, certain frequencies of the light are absorbed, depending on the principal transition of the interaction. In the case of gold, the relevant transition is between the $5d^{10} 6s^2 S_{1/2}$ and $5d^9 6s^2 ^2D_{5/2}$ levels (an *E2* transition; see below) with wavelength 467 nm, which is in the blue region of the visible spectrum. Hence, for gold blue light is absorbed but colours at other frequencies are reflected, particularly the yellow to red wavelengths. Thus, gold has its characteristic golden appearance. If nonrelativistic orbital functions were to be used, the corresponding transition energy would be well outside the visible range and the golden colour would not be predicted. By contrast, the equivalent transition in silver between the $4d^{10} 5s^2 S_{1/2}$ and $4d^9 5s^2 ^2D_{5/2}$ levels is at 328 nm, outside the visible spectral range, and therefore all of the colours of the visible spectrum are reflected. Thus, silver appears metallic grey.

5.2. Transition rates

If we restrict ourselves to *LS* coupling, only electric dipole (*E1*) transitions are possible, and between states of the same

Table 4

 $2s^2\ ^1S_0-2s3p\ ^3P_1^o$ in beryllium-like ions.
$$\Delta E_1 = E(2s3p\ ^3P_1^o) - E(2s^2\ ^1S_0); \Delta E_2 = E(2s3p\ ^1P_1^o) - E(2s3p\ ^3P_1^o).$$

		C III	N IV	O V
Energies (au)				
ΔE_1	Calculated†	1.17568	1.843	2.649
	Experiment‡	1.18333	1.850	2.656
ΔE_2	Calculated†	0.001715	0.00204	0.00480
	Experiment‡	0.003554	0.00668	0.00918
A-values (μs^{-1})				
Experiment§		3.3 ± 2.7	22 ± 6	88 ± 9
	Calculated			
Ab initio¶		2.18	32.7	66.8
	Fine-tuned†	0.51	3.0	18.2
	MCHF¶¶	0.50 ± 0.02	3.2 ± 0.1	19.6 ± 0.4
	GRASP		1.4	16.4

† Hibbert (1979). ‡ Kramida *et al.* (2018). § Engström *et al.* (1979). ¶ Froese Fischer, Gaigalas *et al.* (1997). || Fritzsche & Grant (1994).

spin with their orbital angular momenta satisfying $|L - L'| \leq 1$, with $L = L' = 0$ excluded. Such transitions are normally termed ‘allowed’. The introduction of relativistic effects into the Hamiltonian opens up other possibilities. The coupling of CSFs with different L and S , as in equation (20), means that $E1$ transitions can now include intercombination lines. Normally, such lines have small oscillator strengths or transition rates, but in some cases they can be comparable to those of allowed transitions. An example of this is between the $2s^2\ ^1S_0$ and $2s3p\ ^3P_1^o$ levels in beryllium-like ions, as shown in Table 4. The unusually large A -value of this transition arises because the $2s3p\ ^3P_1^o$ and $^1P_1^o$ levels lie close in energy and so there is stronger than usual mixing between them. The table also exemplifies several other points which have general application. Firstly, it is important to get such energy separations correct, and not just the transition energy. Secondly, fine-tuning can lead to substantial improvements in *ab initio* calculations of transition rates. Thirdly, it allows some comparison between different methods: CIV3 and MCHF (both including Breit–Pauli interactions) and the fully relativistic GRASP. The differences between the three sets of results in Table 4 arise because of the different sizes of the CI expansions, rather than because of intrinsic differences in the methods themselves. It is customarily found that for light elements such as these, a fully relativistic treatment confers no advantages over a method based on the Breit–Pauli approximation, but as the nuclear charge (and more particularly the degree of ionization of the element under consideration) increases the fully relativistic approach is essential. It is often considered that this point is reached at around $Z = 30$, although Spencer *et al.* (2014) found that using CIV3 in the Breit–Pauli approximation, augmented by length contraction within the outer electrons as adopted by Cowan (1981), calculated energy differences and A -values close to those of the GRASP calculations of Ballance & Griffin (2007) were achieved.

In LSJ or $j-j$ coupling, other ‘forbidden’ lines, arising from a theoretical point of view from relativistic interactions, can have a nonzero transition rate. The most commonly encountered are magnetic dipole ($M1$), electric quadrupole ($E2$) and (on occasion) electric or magnetic octupole ($E3$ and $M3$,

Table 5

Oscillator strengths in Fe II.

Wavelength (Å)	K†	RU‡	CH§
2507.552	0.001	0.233	0.138
2509.097	0.297	0.045	0.136
Total	0.298	0.278	0.274

† Kurucz (2003). ‡ Raassen & Uylings (1998). § Corrége & Hibbert (2005).

respectively). The transition mentioned in the previous section, determining the apparent colour of gold, is an example of an electric quadrupole ($E2$) transition.

For lighter ions, their rates are usually several orders of magnitude smaller than allowed transitions. However, as the nuclear charge increases the ‘forbidden’ transition rates increase quickly because they are proportional to high powers of Z (Hibbert, 2011), so that for more highly ionized systems these so-called ‘forbidden’ transitions eventually dominate over the allowed electric dipole transitions (Jacobs, 1972).

The calculation of forbidden transitions is neither harder nor easier than the calculation of $E1$ transitions. Difficulties in the calculations arise because of one or more factors affecting the wavefunctions, particularly the degree of mixing between the wavefunctions of different levels, at times the identification of levels, the extent of the difference between the optimal radial functions of the orbitals and the length of the CI expansion required to capture at least a large part of the electron correlation. CI cancellation effects can have significant effects on the accuracy of the transition rates. The order of the multipole operator ($k = 1, 2, 3 \dots$) involved in the calculation is not usually a large factor in their accuracy.

An alternative measure of the strength of the transition is its (absorption) oscillator strength, a dimensionless quantity that is a multiple of the (emission) transition rate. As an example of the difficulty in the identification of levels, the accuracy needed in the calculation of the energies of the levels and the need to be careful when applying extrapolation techniques such as fine-tuning, in Table 5 we show the oscillator strengths of two neighbouring lines in the emission spectrum of the B and D Weigelt blobs in the star Eta Carinae, as calculated by Kurucz (2003) using the Cowan code, by Raassen & Uylings (1998) using an orthogonal operators method and by Corrége & Hibbert (2005) using CIV3. The results of the three calculations are very different.

The two lines were notionally attributed to the transitions $2507.552: c^4F_{7/2-x^6}F_{9/2}^o$ and $2509.097: c^4F_{7/2-y^4}G_{9/2}^o$. On this basis, the first line is an intercombination line which should have a much smaller oscillator strength than the second line, which is an allowed line. That is what Kurucz found. However, Raassen and Uylings found the first line to be stronger than the second line. In our calculation (Corrége & Hibbert, 2005), our oscillator strengths are approximately equal. We also found that the upper-level wavefunctions are heavily mixed between the two upper-state labels but also with $5p\ ^4P^o$, and that the relative sizes of the oscillator strengths are directly related to the amount of the $^4G_{9/2}^o$ configuration in the upper levels. Our values were confirmed by observations by Verner *et al.* (2002). Since the different authors calculate similar

values for the sum of the two oscillator strengths, it is clear that these quite substantial differences arise because of the redistribution of the oscillator strength between the two transitions.

This result points to the need to be careful in evaluating calculated oscillator strengths. Unlike the calculation of energies, there is no useful variational principle which would allow us to show that a larger calculation should improve the values. Instead, we have to rely on indicators of accuracy (Hibbert, 1996), which we take into account in our assessment: ideally, a sequence of calculations of systematically increasing complexity, some apparent convergence of the oscillator strengths for this sequence, for allowed transitions a comparison between length and velocity forms of the oscillator strengths, and wherever possible a comparison with experiment or observation. There is therefore a need for theorists and experimentalists to work together constructively.

References

- Badnell, N. R. (1986). *J. Phys. B At. Mol. Phys.* **19**, 3827–3835.
- Ballance, C. P. & Griffin, D. C. (2007). *J. Phys. B At. Mol. Opt. Phys.* **40**, 247–258.
- Bethe, H. A. & Salpeter, E. E. (1957). *Quantum Mechanics of One- and Two-Electron Atoms*. Berlin, Heidelberg: Springer.
- Bransden, B. H. & Joachain, C. J. (1983). *Physics of Atoms and Molecules*. London, New York: Longman.
- Bunge, C. (1970). *Theor. Chim. Acta*, **16**, 126–144.
- Cassidy, C. M., Hibbert, A. & Ramsbottom, C. A. (2016). *Astron. Astrophys.* **587**, A107.
- Chantler, C. T., Nguyen, T. V. B., Lowe, J. A. & Grant, I. P. (2014). *Phys. Rev. A*, **90**, 062504.
- Clementi, E. & Roetti, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177–478.
- Corr g , G. & Hibbert, A. (2005). *Astrophys. J.* **627**, L157–L159.
- Cowan, R. D. (1981). *The Theory of Atomic Structure and Spectra*. Berkeley: University of California Press.
- Cowan, R. D. & Griffin, D. C. (1976). *J. Opt. Soc. Am.* **66**, 1010–1014.
- Desclaux, J. P. (1975). *Comput. Phys. Commun.* **9**, 31–45.
- Dirac, P. A. M. (1928a). *Proc. R. Soc. Lond. A*, **117**, 610–624.
- Dirac, P. A. M. (1928b). *Proc. R. Soc. Lond. A*, **118**, 351–361.
- Dyall, K. G., Grant, I. P., Johnson, C. T., Parpia, F. A. & Plummer, E. P. (1989). *Comput. Phys. Commun.* **55**, 425–456.
- Eissner, W., Jones, M. & Nussbaumer, H. (1974). *Comput. Phys. Commun.* **8**, 270–306.
- Engstr m, L., Denne, B., Hultdt, S., Ekberg, J. O., Curtis, L. J., Veje, E. & Martinson, I. (1979). *Phys. Scr.* **20**, 88–92.
- Fock, V. (1930). *Z. Phys.* **61**, 126–148.
- Fritzsche, S. & Grant, I. P. (1994). *Phys. Scr.* **50**, 473–480.
- Froese Fischer, C. (1970). *Comput. Phys. Commun.* **1**, 151–166.
- Froese Fischer, C. (1977). *The Hartree–Fock Method for Atoms: A Numerical Approach*. New York: John Wiley & Sons.
- Froese Fischer, C. (1978). *Comput. Phys. Commun.* **14**, 145–153.
- Froese Fischer, C. (1991). *Comput. Phys. Commun.* **64**, 369–398.
- Froese Fischer, C., Brage, T. & J nsson, P. (1997). *Computational Atomic Structure. An MCHF Approach*. Bristol: Institute of Physics.
- Froese Fischer, C., Gaigalas, G. & Godefroid, M. R. (1997). *J. Phys. B At. Mol. Opt. Phys.* **30**, 3333–3342.
- Grant, I. P. (2007). *Relativistic Quantum Theory of Atoms and Molecules*. New York: Springer.
- Grant, I. P., McKenzie, B. J., Norrington, P. H., Mayers, D. F. & Pyper, N. C. (1980). *Comput. Phys. Commun.* **21**, 207–231.
- Hartree, D. R. (1928a). *Math. Proc. Camb. Phil. Soc.* **24**, 89–110.
- Hartree, D. R. (1928b). *Math. Proc. Camb. Phil. Soc.* **24**, 111–132.
- Hartree, D. R. (1957). *The Calculation of Atomic Structures*. New York: Wiley.
- Hartree, D. R. & Hartree, W. (1936). *Proc. R. Soc. Lond. A*, **156**, 45–62.
- Hibbert, A. (1975). *Comput. Phys. Commun.* **9**, 141–172.
- Hibbert, A. (1979). *J. Phys. B At. Mol. Phys.* **12**, L661–L665.
- Hibbert, A. (1996). *Phys. Scr.* **196**, 104–109.
- Hibbert, A. (2011). *Handbook for Highly Charged Ion Spectroscopic Research*, edited by Y. Zou, R. Hutton, F. Currell, I. Martinson & S. Hagmann, pp. 169–182. Boca Raton: CRC Press.
- Hibbert, A., Glass, R. & Froese Fischer, C. (1991). *Comput. Phys. Commun.* **64**, 455–472.
- Hibbert, A., Ojha, P. C. & Stafford, R. P. (1992). *J. Phys. B At. Mol. Opt. Phys.* **25**, 4153–4162.
- Hylleraas, E. A. (1929). *Z. Phys.* **54**, 347–366.
- Hylleraas, E. A. & Undheim, B. (1930). *Z. Phys.* **65**, 759–772.
- Indelicato, P., Boucard, S. & Lindroth, E. (1998). *Eur. Phys. J. D At. Mol. Opt. Phys.* **3**, 29–41.
- Jacobs, V. L. (1972). *J. Phys. B At. Mol. Phys.* **5**, 213–217.
- J nsson, P., Gaigalas, G., Biero n, J., Froese Fischer, C. & Grant, I. P. (2013). *Comput. Phys. Commun.* **184**, 2197–2203.
- Kramida, A., Ralchenko, Y. & Reader, J. (2018). *Atomic Spectra Database*, version 5.5.6. Gaithersburg: National Institute of Standards and Technology. <https://physics.nist.gov/asd>.
- Kurucz, R. L. (2003). *Kurucz/Atoms*. <http://kurucz.harvard.edu/atoms.html>.
- Lowe, J. A., Chantler, C. T. & Grant, I. P. (2013). *Radiat. Phys. Chem.* **85**, 118–123.
- MacDonald, J. K. L. (1933). *Phys. Rev.* **43**, 830–833.
- Martin, W. C. & Zalubas, R. (1983). *J. Phys. Chem. Ref. Data*, **12**, 323–380.
- Mohan, M. & Hibbert, A. (1987). *J. Phys. B At. Mol. Phys.* **20**, 907–918.
- Nicolaides, C. A. & Beck, D. R. (1975). *Chem. Phys. Lett.* **36**, 79–85.
- Parpia, F. A., Froese Fischer, C. & Grant, I. P. (1996). *Comput. Phys. Commun.* **94**, 249–271.
- Raassen, A. J. J. & Uylings, P. H. M. (1998). *J. Phys. B At. Mol. Opt. Phys.* **31**, 3137–3146.
- Roothaan, C. C. J. (1951). *Rev. Mod. Phys.* **23**, 69–89.
- Schr dinger, E. (1926). *Ann. Phys.* **77**, 361–376.
- Slater, J. C. (1930). *Phys. Rev.* **35**, 210–211.
- Spencer, S., Hibbert, A. & Ramsbottom, C. A. (2014). *J. Phys. B At. Mol. Opt. Phys.* **47**, 245001.
- Verner, E. M., Gull, T. R., Bruhweiler, F., Johansson, S., Ishibashi, K. & Davidson, K. (2002). *Astrophys. J.* **581**, 1154–1167.
- Welton, T. A. (1948). *Phys. Rev.* **74**, 1157–1167.