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A semiclassical formula for the term energy of a many-electron atom

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Abstract. A semiclassical formulation for the term energy of a many-electron atom is presented which includes gross structure, fine structure, core polarisation and core penetration effects. A very simple model combining perturbed Keplerian orbits with the Bohr–Sommerfeld–Wilson quantisation hypothesis yields an explicit formula which, in appropriate limits, reduces to the familiar core polarisability and quantum defect parametrisations. The formula also provides a new parametrisation in terms of an effective core charge within an effective core radius, which has been applied to predict higher term values in the 3s*n*g states of Si III.

1. Introduction

Spectroscopic determination of atomic energy levels in many-electron atoms is often aided by the use of empirical parametrisations based on simple semiclassical one-electron models. The high precision of optical spectroscopic measurements exceeds present capabilities for *ab initio* many-electron calculations, and empirical interpolations and extrapolations of measured data among similar atomic systems can sometimes provide more accurate predictions. A common approach is to describe the active electron in a complex atom in terms of a quasi-hydrogen-like model with some parametrised perturbation to account for the presence of the passive electrons. By transforming measured wavelength data into values for these empirical parameters, regularities among similar systems are sometimes revealed. A familiar example of this approach is found in the Rydberg–Ritz many-electron parametrisation of the hydrogenic Balmer formula. Obviously such models cannot adequately include effects such as configuration interaction and exchange, but the importance of such effects in a particular application is clearly shown by the degree of regularity present when a parametrisation is attempted.

Prior to the development of modern quantum mechanics, vigorous efforts were made to explore the origins of these empirical regularities. Attempts were made (e.g., Schrödinger 1921, Wentzel 1923, van Urk 1923, Born 1927) to deduce symbolic formulae for quantum defects, core polarisation and core penetration energies, screening parameters, etc, using the old quantum theory (combining Newtonian mechanics with the Bohr–Sommerfeld–Wilson quantisation hypothesis). However, the resultant action integrals were mathematically complicated and provided limited insight into the basic physical processes. In the period 1924–26 the old quantum theory was thought to be totally inadequate to describe such things as many-electron atoms, molecules,

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electron spin, etc, and it was replaced by the completely new approaches of Heisenberg and Schrödinger. Since modern quantum mechanics makes possible the use of numerical brute force in the solution of complicated problems, the formal semiclassical approach was largely abandoned, except in empirical applications such as those in atomic spectroscopy. Recently there has been a revival of the use of formal semi-empirical theories to supplement numerical calculations, and modern versions of the old quantum theory have been successfully applied to problems for which it seemed to fail in the 1920's (e.g., Leopold *et al* 1980, Leopold and Percival 1980).

The purpose of this paper is twofold: firstly, to provide insight by showing how the semi-empirical formulae can be traced back to a semiclassical model in a clear and intuitive manner, and secondly, to provide a simple model which can be used to parametrise empirical data to aid in the classification of spectra. This formulation utilises simple time averages of powers of the radii of Keplerian orbits and the Bohr–Sommerfeld–Wilson quantisation hypothesis, and includes gross structure, fine structure, core polarisation and core penetration effects. The method leads to an explicit formula for the term energy, provides an exposition of the physical basis of the spectroscopic core polarisation formula and the Rydberg–Ritz quantum defect parametrisation, and yields a new means of parametrising core penetration effects which is useful in classifying spectral measurements.

2. Spectroscopic term energy

High precision spectroscopic term analyses of complex atoms are sometimes expedited through the use of parametrised semiclassical one-electron models. A Coulomb potential is often used as a zeroth approximation, with perturbations described using hydrogenic expectation values. This approach is well suited to the description of closed-shell core systems and also can be applied to higher excited states in open-shell core systems. Even when the approach breaks down, e.g., due to exchange effects, configuration interaction, etc, it can be useful in identifying the states for which these effects are strong. The methods of calculation vary in their sophistication and primary consideration here will be to those spectroscopic procedures which have been comprehensively described by Edlén (1964).

The term energy T (measured relative to the ionisation limit) of an outer active electron orbiting a core, consisting of a nucleus and deformable cloud of inner passive electrons with effective charge ζ and dipole and quadrupole polarisabilities α_d and α_q, can be written as

$$T = Ra_0[\langle \zeta r^{-1} \rangle + \alpha^2 a_0(\langle \zeta^2 r^{-2} \rangle - \tfrac{3}{4}\langle \zeta r^{-1} \rangle^2) - \alpha^2 a_0^2 \langle (\boldsymbol{l} \cdot \boldsymbol{s}) \zeta r^{-3} \rangle + \langle \alpha_d r^{-4} \rangle + \langle \alpha_q r^{-6} \rangle]. \quad (1)$$

Here R is the Rydberg constant, a_0 is the Bohr radius, α is the fine-structure constant and l and s are the orbital and spin angular momentum quantum numbers. The first contribution corresponds to the total non-relativistic energy for a spherically symmetric core, written in terms of r^{-1} using the classical virial theorem. The second contribution is the relativistic correction to the kinetic energy (cf Woodgate 1970, p 58). The contribution involving r^{-3} is the spin–orbit magnetic interaction, corrected for the Thomas precession (cf Woodgate 1970, pp 59–60). Evaluation of $\boldsymbol{l} \cdot \boldsymbol{s}$ can be made semiclassically by use of the vector model. (The relativistic kinetic energy correction

and the spin–orbit magnetic interaction together comprise the fine-structure energy.) The contributions involving r^{-4} and r^{-6} represent the energies arising from the interaction of the active electron with dipole and quadrupole moments induced in the core electron configurations (Edlén 1964). If equation (1) describes a 'non-penetrating' orbit, the quantities ζ, α_d and α_q are constant over the orbit and can be factored outside of the averages. If the orbit penetrates the core, these quantities vary over the orbit (note that for a potential of the form $\zeta(r)/r$ both the virial theorem and the spin–orbit magnetic field operator introduce additional potential gradient factors involving $d\zeta/dr$ which have, for simplicity, been neglected in equation (1)).

In the quantum mechanical formulation the bracketed average values in equation (1) refer to expectation values. In the semiclassical approach used here these will instead be interpreted to represent time averages over the classical Keplerian orbit.

3. Mean powers of weighted Keplerian radii

The integrals which occur in equation (1) are of the form

$$\langle \gamma r^s \rangle = \left(\int_0^\tau dt\, r^s \gamma \right) \left(\int_0^\tau dt \right)^{-1}$$
$$= \left(\int_0^{2\pi} d\phi \left(\frac{d\phi}{dt} \right)^{-1} r^s \gamma \right) \left[\int_0^{2\pi} d\phi \left(\frac{d\phi}{dt} \right)^{-1} \right]^{-1} \tag{2}$$

where τ is the period of the orbit and γ represents the local value of ζ, α_d or α_q as a function of position on the orbit. The values $s = -1, -2, -3, -4$ and -6 are needed for equation (1). For an unperturbed Coulomb potential (the perturbed orbits precess and are not closed), an orbit of radius r and azimuthal angle ϕ about the principal focus is described by Kepler's three laws

$$1/r = (1 + \varepsilon \cos \phi)/a(1 - \varepsilon^2) \tag{3}$$

$$r^2\, d\phi/dt = 2\pi a^2 (1 - \varepsilon^2)^{1/2}/\tau \tag{4}$$

$$\tau = 2\pi (m a^3/\zeta e^2)^{1/2} \tag{5}$$

where a and ε are the length of the semi-major axis and the eccentricity of the ellipse, and τ is written in terms of the electrostatic central force (in atomic units $e^2/m = \alpha^2 c^2 a_0$). Thus equation (2) can be rewritten

$$\langle \gamma r^s \rangle = \frac{\int_0^{2\pi} d\phi (1 + \varepsilon \cos \phi)^{-s-2} [a(1 - \varepsilon^2)]^{s+3/2} \gamma/\zeta^{1/2}}{\int_0^{2\pi} d\phi (1 + \varepsilon \cos \phi)^{-2} [a(1 - \varepsilon^2)]^{3/2}/\zeta^{1/2}} \tag{6}$$

where a, ε, ζ and γ have been left inside the integrals since they will vary with ϕ if core penetration occurs. In the standard Bohr–Sommerfeld–Wilson quantisation, orbits occur only under the conditions

$$a = a_0 n^2/\zeta \tag{7}$$

$$(1 - \varepsilon^2)^{1/2} = k/n \tag{8}$$

where n is the principal quantum number and k is the quantum number corresponding to angular momentum in the old quantum theory (cf White 1934). Here we shall adopt a simple model for penetration in which the central charge has a constant value ζ_c in the

internal region $r<\rho$ and a constant value ζ in the external region $r>\rho$. If penetration occurs the effective principal quantum numbers, semi-major axes and eccentricities will differ in the internal and external regions, but the angular momentum and total energy will be constant over the orbit. There will be an effective precession of the penetrating orbit, since it involves the connection of orbit segments of differing a and ε. Although the motion is not periodic, long-term average values for the precessing penetrating orbits can be computed by joining orbit segments to form a complete cycle in the precessing frame.

3.1. Non-penetrating orbits

If the orbital electron does not penetrate the core, then the effective value for ζ is equal to the net core charge (nuclear charge minus the number of core electrons) over the entire orbit and α_d and α_q are also constant over the orbit. Thus the quantities γ, a, ε and τ can be moved outside the integral, leaving

$$\langle r^s\rangle = a^s(1-\varepsilon^2)^{s+3/2}\int_0^{\pi} d\phi\ (1+\varepsilon\cos\phi)^{-s-2}/\pi \tag{9}$$

which can be performed analytically (Gradshteyn and Ryzhik 1965, formulae 3.661(3) and 3.661(4)) to yield a general expression, valid for the average value of any power of r for a Keplerian orbit, which is

$$\langle r^s\rangle = a^s(1-\varepsilon^2)^{s/2+1/2}P_{|s+3/2|-1/2}[1/(1-\varepsilon^2)^{1/2}]. \tag{10}$$

Here $P_q(x)$ is the Legendre polynomial (the order q has been expressed as manifestly positive in equation (10) through the relationship $P_{-q}(x)=P_{q-1}(x)$). Using the quantisation conditions of equations (7) and (8), this becomes

$$\langle r^s\rangle = (a_0n^2/\zeta)^s(k/n)^{s+1}P_{|s+3/2|-1/2}(n/k) \tag{11}$$

and the average values in equation (1) are given by

$$\langle r^{-1}\rangle = (\zeta/a_0)/n^2 \tag{12}$$

$$\langle r^{-2}\rangle = (\zeta/a_0)^2/n^3k \tag{13}$$

$$\langle r^{-3}\rangle = (\zeta/a_0)^3/n^3k^3 \tag{14}$$

$$\langle r^{-4}\rangle = (\zeta/a_0)^4(3-k^2/n^2)/2n^3k^5 \tag{15}$$

$$\langle r^{-6}\rangle = (\zeta/a_0)^6(35-30k^2/n^2+3k^4/n^4)/8n^3k^9. \tag{16}$$

It is well known that these average values are very similar to the quantum mechanical results (Bockasten 1974). They can be made to correspond exactly if appropriate substitutions are made for the average values of powers of k. If factored as in equations (12)–(16) (so that the numerator is an ascending even power series in k/n starting with zeroth power), odd powers of k are replaced by

$$k^{2q+1} = (2l+q+1)!/(2l-q)!2^{2q+1}. \tag{17}$$

For even powers of k the replacement is more complicated, since it depends upon the order λ of the Legendre polynomial, and can be written as

$$k^{2q} = \sum_{i=0}^{q}(-1)^{q+i}C_{\lambda qi}(l+i)!/(l-i)! \tag{18}$$

where the coefficients $C_{\lambda qi}$ are positive rational fractions which can be evaluated by inspection of the quantum mechanical expressions (Bockasten 1974) and are listed for $\lambda \leqslant 6$ in table 1. It has long been known (Fock 1935) that the radial equation of the hydrogen atom possesses O(4) symmetry, and thus has group theoretical properties similar to those of angular momentum (the principal quantum number of the radial formulation behaves like the magnetic quantum number of angular momentum). The results obtained above contain evidence of that symmetry, since powers of k are no longer interpreted as successive algebraic multiplications but are instead replaced by the substitutions of equations (17) and (18). Reduction to the semiclassical limit thus occurs if k is interpreted as a normal algebraic multiplicative operator.

Table 1.

		$C_{\lambda qi}$			
λ	q	$i=0$	$i=1$	$i=2$	$i=3$
2	1	0	1		
3	1	$\frac{1}{3}$	1		
4	1	$\frac{5}{6}$	1		
4	2	0	0	1	
5	1	$\frac{3}{2}$	1		
5	2	$\frac{4}{5}$	$\frac{4}{3}$	1	
6	1	$\frac{7}{3}$	1		
6	2	$\frac{14}{5}$	3	1	
6	3	0	0	0	1

Several interesting insights can be gained by inspection of equation (11). For example, it can easily be seen that $\langle r^{-s}\rangle$ is independent of k only in the two cases $s=0$ and $s=-1$. Thus (excluding the trivial case of the norm) the $1/r$ case is unique in the fact that its average value is independent of k, providing an exposition of the familiar 'accidental degeneracy' peculiar to the Coulomb potential. Since a Legendre polynomial of order q occurs in equation (11) for both $s=-q-2$ and for $s=q-1$ (originating in the relationship $P_{-i}(x)=P_{i-1}(x)$) the two corresponding average values have the relationship

$$\langle r^{-q-2}\rangle = \langle \zeta/a_0 nk\rangle^{2q+1}\langle r^{q-1}\rangle \tag{19}$$

which, with the substitution of equation (17), yields a known quantum mechanical identity (Pasternak 1937). This symmetry of Legendre polynomial orders about the point $s=-\frac{3}{2}$ breaks equation (11) into two families of solutions with respect to the asymptotic behaviour of $\langle r^s\rangle$ along a Rydberg series. For fixed k and increasing n the quantity n/k becomes large, in which case $P_q(n/k)\propto(n/k)^q$, resulting in the asymptotic dependence for $n \gg k$

$$\langle r^s\rangle \propto \begin{cases} n^{2s} & s \geqslant -1 \\ n^{-3}k^{2s+3} & s \leqslant -2 \end{cases} \tag{20}$$

which is equally valid in the quantum mechanical formulation. Thus, for large n, the average values of positive powers of r do not depend on k (an asymptotic analogue of the accidental degeneracy), and the average values of quadratic and higher powers of the reciprocal of r all have the same functional dependence upon n. As will be discussed in § 4.1, it is very difficult to determine dipole and quadrupole polarisabilities using spectroscopic term analysis data from a single Rydberg series, a direct consequence of the similarity of the n dependences of $\langle r^{-4}\rangle$ and $\langle r^{-6}\rangle$.

3.2. Penetrating orbits

If the orbit penetrates the core, γ, a and ε are not constant over the orbital path, but are functions of the integration variable ϕ. The simplest useful model of the core ascribes to it a well defined radius ρ, within which the effective charge ζ_c is constant and the dipole and quadrupole polarisabilities vanish, and neglects external screening. In this case the orbit segment within the core will have values for its semi-major axis a_c, eccentricity ε_c and period τ_c different from those of the external segment. Penetration will occur if ρ exceeds the externally computed distance of closest approach but is less than the distance of greatest retreat

$$a(1-\varepsilon)<\rho<a(1+\varepsilon). \tag{21}$$

The angle Φ at which penetration occurs can be seen from equation (3) to be given by

$$\cos\Phi=[(1-\varepsilon^2)a/\rho-1]/\varepsilon. \tag{22}$$

In terms of the internal orbit this angle has a different value Φ_c, given by

$$\cos\Phi_c=[(1-\varepsilon_c^2)a_c/\rho-1]/\varepsilon_c. \tag{23}$$

This arises from the fact that the internal and external orbit ellipses have non-collinear major axes, which leads to an effective precession per completed orbit of $2(\Phi_c-\Phi)$. Since the true orbit is not closed, we define the average value as twice the integral from perihelion to aphelion, which, owing to this precession, does not correspond to a revolution in a stationary (non-precessing) reference frame.

The internal and external orbit parameters can be related by conservation of energy and angular momentum, which must be the same for the valence electron whether it is inside or outside of the core. If, at this step, we approximate the energy by a model which includes the core charge but not the core polarisation, this corresponds to a spherical shell of charge which adds a constant potential to the internal region. Using the virial theorem to relate the potential energy to the total energy, this provides a relationship between the internal and external semi-major axes

$$-\zeta/2a=-\zeta_c/2a_c+(\zeta_c-\zeta)/\rho \tag{24}$$

which, through equation (7), relates the internal and external effective principal quantum numbers. (In the proper use of the Bohr–Sommerfeld–Wilson quantisation, the principal quantum number is equated to the action integral over both regions. Here, using a perturbation approach, we assume that the external quantum number n is well represented by an integer, but allow the internal quantum number to be non-integer.) Equation (24) can be rewritten in a symmetric form showing that the quantity (the energy relative to the aphelion of an S state)

$$\zeta(2-\rho/a)=\zeta_c(2-\rho/a_c) \tag{25}$$

is an invariant over the two regions. The length of the internal semi-major axis is given by

$$a_c = a\zeta_c\rho/[2(\zeta_c - \zeta)a + \zeta\rho]. \tag{26}$$

Similarly, the orbital angular momentum L

$$L = 2\pi m a^2(1-\varepsilon^2)^{1/2}/\tau \tag{27}$$

(and its corresponding quantum number k) is constant over the orbit, and using equation (5), can be rewritten

$$L^2/me^2 = \zeta a(1-\varepsilon^2) = \zeta_c a_c(1-\varepsilon_c^2) \tag{28}$$

yielding another invariant over the two regions and providing a relationship for the internal eccentricity, which, from equation (26), is

$$(1-\varepsilon_c^2) = (1-\varepsilon^2)[2(\zeta_c - \zeta)a + \zeta\rho]\zeta/\zeta_c^2\rho. \tag{29}$$

Since both the desired average value and the effective value of the period τ_{eff} depend upon the internal and external regions, equation (2) must be broken up into segmental integrals in both numerator and denominator. Thus

$$\tau_{\text{eff}} = 2\int_0^{\Phi_c} [\mathrm{d}t]_{\text{int}} + 2\int_{\Phi}^{\pi} [\mathrm{d}t]_{\text{ext}} \tag{30}$$

and

$$\langle \gamma r^s \rangle = \left(2\gamma_c \int_0^{\Phi_c} [\mathrm{d}t\, r^s]_{\text{int}} + 2\gamma \int_{\Phi}^{\pi} [\mathrm{d}t\, r^s]_{\text{ext}}\right)\tau_{\text{eff}}^{-1} \tag{31}$$

where the subscripted brackets indicate that appropriate segmental values for a and ε are used for the internal and external regions. Equations (30) and (31) can be rewritten in terms of the non-penetrating case by adding and subtracting a fictional integral from $\phi = 0$ to $\phi = \Phi$ which employs the external orbit constants to yield

$$\begin{aligned}\tau_{\text{eff}} &= 2\int_0^{\Phi_c} [\mathrm{d}t]_{\text{int}} + 2\int_0^{\pi} [\mathrm{d}t]_{\text{ext}} - 2\int_0^{\Phi} [\mathrm{d}t]_{\text{ext}} \\ &= \tau(1 + \ell_c(0) - \ell(0))\end{aligned} \tag{32}$$

and

$$\begin{aligned}\langle \gamma r^s \rangle &= \left(2\gamma_c \int_0^{\Phi_c} [\mathrm{d}t\, r^s]_{\text{int}} + 2\gamma \int_0^{\pi} [\mathrm{d}t\, r^s]_{\text{ext}} - 2\gamma \int_0^{\Phi} [dt\, r^s]_{\text{ext}}\right)\tau_{\text{eff}}^{-1} \\ &= \gamma\langle r^s \rangle_{\text{ext}}[1 + (\gamma_c/\gamma)\ell_c(s) - \ell(s)]\tau/\tau_{\text{eff}}\end{aligned} \tag{33}$$

where $\langle r^s \rangle_{\text{ext}}$ is the result obtained from equation (10) and $\ell_m(s)$ is given by

$$\ell_m(s) = \left(\frac{\zeta}{\zeta_m}\right)^{s+2}\left(\int_0^{\Phi_m} \mathrm{d}\phi\ (1+\varepsilon_m\cos\phi)^{-s-2}\right)\left(\int_0^{\pi} \mathrm{d}\phi\ (1+\varepsilon\cos\phi)^{-s-2}\right)^{-1}. \tag{34}$$

Here m → c and m → no subscript denote, respectively, the internal and external regions. (Ratios of factors involving a, ε, a_c and ε_c reduce to the charge ratio factor from equation (28).) The integrals in equation (34) can be performed analytically (Gradshteyn and Ryzhik 1965, Robson 1967) and are listed for the desired values of s in

table 2. Penetration corrections can thus be effected by a multiplicative factor

$$\langle \gamma r^s \rangle = (1+f_{-s})\gamma \langle r^s \rangle_{\text{ext}} \tag{35}$$

where

$$f_{-s} = [(\gamma_c/\gamma)\ell_c(s) - \ell_c(0) - \ell(s) + \ell(0)]\tau/\tau_{\text{eff}}. \tag{36}$$

Table 2.

s	$\int_0^{\Phi} d\phi\,(1+\varepsilon\cos\phi)^{-s-2}$
0	$\frac{1}{1-\varepsilon^2}\left[\frac{1}{(1-\varepsilon^2)^{1/2}}\tan^{-1}\left(\frac{(1-\varepsilon^2)^{1/2}\sin\Phi}{\varepsilon+\cos\Phi}\right)-\frac{\varepsilon\sin\Phi}{1+\varepsilon\cos\Phi}\right]$
−1	$\frac{1}{(1-\varepsilon^2)^{1/2}}\tan^{-1}\left(\frac{(1-\varepsilon^2)^{1/2}\sin\Phi}{\varepsilon+\cos\Phi}\right)$
−2	Φ
−3	$\Phi+\varepsilon\sin\Phi$
−4	$(1+\frac{1}{2}\varepsilon^2)\Phi+2\varepsilon\sin\Phi+\frac{1}{2}\varepsilon^2\sin\Phi\cos\Phi$
−6	$(1+3\varepsilon^2+\frac{3}{8}\varepsilon^4)\Phi+4\varepsilon(1+\varepsilon^2)\sin\Phi+3\varepsilon^2(1+\frac{1}{8}\varepsilon^2)\sin\Phi\cos\Phi-\frac{4}{3}\varepsilon^3\sin^3\Phi+\frac{1}{4}\varepsilon^4\sin\Phi\cos^3\Phi$

4. Results

Using the computations of § 3, the term value of equation (1) can be written as

$$T = T_{\text{non}} + T_{\text{pen}} \tag{37}$$

where T_{non} is the non-penetrating portion, given by

$$T_{\text{non}} = R\left[\frac{\zeta^2}{n^2}+\frac{\alpha^2\zeta^4}{n^3}\left(\frac{1}{k}-\frac{3}{4n}-\frac{\langle \boldsymbol{l}\cdot\boldsymbol{s}\rangle}{k^3}\right)+\frac{\alpha_d}{a_0^3}\frac{\zeta^4}{2n^3k^5}\left(3-\frac{k^2}{n^2}\right)\right.$$
$$\left.+\frac{\alpha_q}{a_0^5}\frac{\zeta^6}{8n^3k^9}\left(35-30\frac{k^2}{n^2}+3\frac{k^4}{n^4}\right)\right] \tag{38}$$

and T_{pen} is the penetrating portion, given by

$$T_{\text{pen}} = R\left[\frac{\zeta^2}{n^2}f_1+\frac{\alpha^2\zeta^4}{n^3k}f_2-\frac{3\alpha^2\zeta^4}{4n^4}f_1(2-f_1)-\frac{\alpha^2\zeta^4\langle \boldsymbol{l}\cdot\boldsymbol{s}\rangle}{n^3k^3}f_3\right.$$
$$\left.+\frac{\alpha_d}{a_0^3}\frac{\zeta^4}{2n^3k^5}\left(3-\frac{k^2}{n^2}\right)f_4+\frac{\alpha_q}{a_0^5}\frac{\zeta^6}{8n^3k^9}\left(35-30\frac{k^2}{n^2}+3\frac{k^4}{n^4}\right)f_6\right]. \tag{39}$$

Equation (38) is equivalent to the quantum mechanical result if the various powers of k are replaced by equations (17) and (18), and the substitution

$$\langle \boldsymbol{l}\cdot\boldsymbol{s}\rangle = \tfrac{1}{2}[j(j+1)-l(l+1)-s(s+1)] \tag{40}$$

is made, where j is the total angular momentum quantum number. In the penetrating portion, the same substitutions can be made, and the quantities f_{-s} can be evaluated using equations (22), (23), (34), (36) and table 2. Notice that the fine structure contains

three different radial dependences and thus three different penetration corrections ($s = -1, -2$ and -3), although only one ($s = -3$) depends upon the quantum number j.

4.1. Non-penetrating orbits—the spectroscopic core polarisation formula

The standard approach to the determination of dipole and quadrupole polarisabilities from non-penetrating spectroscopic data is to treat α_d and α_q as undetermined parameters in equation (38) which are fitted to the experimental term values T_{meas} for a given atomic ion. This is often done by a linearising procedure in which the corresponding hydrogen-like term value T_H (i.e., equation (38) with $\alpha_d = \alpha_q = 0$) is subtracted from T_{meas} and the difference divided by $\langle r^{-4}\rangle$ to yield the linear relationship (Edlén 1964, pp 125–9)

$$(T_{meas} - T_H)/Ra_0\langle r^{-4}\rangle = \alpha_d + \alpha_q\langle r^{-6}\rangle/\langle r^{-4}\rangle. \tag{41}$$

A straight-line fit to the data plotted with the expression on the left-hand side of equation (41) as the ordinate and $\langle r^{-4}\rangle/\langle r^{-6}\rangle$ as the abscissa yields α_d and α_q as the intercept and slope. An example of this technique is shown in figure 1 (Toresson 1960). However, if we examine the dependence of this abscissa over the various (n, k) states,

$$\frac{\langle r^{-6}\rangle}{\langle r^{-4}\rangle} = \left(\frac{\zeta}{2a_0}\right)^2 \frac{(35 - 30k^2/n^2 + 3k^4/n^4)}{(3 - k^2/n^2)k^9/k^5} \tag{42}$$

we see that there is only a very weak dependence upon n (due to the fact that all reciprocal powers of r greater than one approach the same n^{-3} dependence with large n). Thus for a given Rydberg series the data points tend to cluster about a narrow range of abscissae on this plot (as seen in figure 1), giving a poor specification of the intercept and slope. This illustrates clearly how important it is that data from several Rydberg series in a given ion are used in this analysis, so that the much stronger k^{-4} dependence in equation (42) leads to widely separated abscissae on the plot, which accurately determine the intercept and slope.

4.2. Highly penetrating orbits—asymptotic form of corrections to the Coulomb energy for low angular momentum states

Since the r^{-1} contribution to equation (1) comprises the dominant portion of the term energy, it often corresponds to the largest penetration corrections to the term energy as well. The penetration correction factor f_1 can, after some algebraic simplification, be written as

$$f_1 = \left(1 - \frac{\zeta a_c}{\zeta_c a}\right)\left[\left(\frac{\zeta_c a_c}{\zeta a}\right)^{1/2} \tan^{-1}\left(\frac{(1-\varepsilon_c^2)^{1/2}\chi}{1-\rho/a_c}\right) - (1-\varepsilon^2)^{1/2}\chi\right]\frac{\tau}{\pi\tau_{eff}} \tag{43}$$

where

$$\chi \equiv [(\rho/a)(2-\rho/a)/(1-\varepsilon^2) - 1]^{1/2} \tag{44}$$

is a quantity which has the same value on both the internal and external segments of the orbit. If we consider situations where very heavy charge penetration occurs ($\zeta_c \gg \zeta$), then the argument of the arc tangent in equation (43) is small and negative, and this function can be approximated by $\tan^{-1} x \simeq \pi + x$, and equation (43) becomes

$$f_1 \simeq \left(1 - \frac{\zeta a_c}{\zeta a}\right)\left[\left(\frac{\zeta_c a_c}{\zeta a}\right)^{1/2} - \left(\frac{\rho/a_c}{\rho/a_c - 1}\right)\frac{(1-\varepsilon^2)^{1/2}\chi}{\pi}\right]\frac{\tau}{\tau_{eff}}. \tag{45}$$

From equation (26) we can see that in the extreme limit of large ζ_c, we can make the replacement $a_c \to \rho/2$. If we further restrict consideration to low angular momentum states so that $\rho \gg a(1-\varepsilon^2)^{1/2}$, and to high principal quantum numbers so that $\rho \ll a$, then equation (45) can be binomially expanded (and written in terms of n using equation (7)),

$$f_1 \simeq \frac{1}{n}\left(\frac{\zeta\rho}{2a_0}\right)^{1/2}\left\{\left[\left(\frac{\zeta_c}{\zeta}\right)^{1/2}-\frac{4}{\pi}\right]+\left(\frac{\zeta\rho}{\pi a_0}\right)\frac{1}{n^2}\right\}\frac{\tau}{\tau_{\text{eff}}}. \tag{46}$$

Thus, neglecting the corrections to the total effective lifetime τ_{eff}, the leading penetration correction is of the form

$$Ra_0(\langle\zeta r^{-1}\rangle-\zeta\langle r^{-1}\rangle)\simeq R\frac{\zeta^2}{n^3}\left\{\left[\left(\frac{\zeta_c\rho}{2a_0}\right)^{1/2}-\frac{4}{\pi}\left(\frac{\zeta\rho}{2a_0}\right)^{1/2}\right]+\frac{2}{\pi}\left(\frac{\zeta\rho}{2a_0}\right)^{3/2}\frac{1}{n^2}\right\}. \tag{47}$$

4.3. Penetrating and non-penetrating orbits—the Rydberg–Ritz quantum defect formulation

With the exception of the Coulomb energy, the leading terms in all of the contributions to equation (37) are proportional to n^{-3}. This similarity in dependence upon principal quantum number of the fine structure, the dipole core polarisability, the quadrupole core polarisability and the core penetration energies is the origin of the success of Rydberg's many-electron extension of the hydrogenic Balmer formula. There the term energy is parametrised by a quantum defect δ, through its definition in the equation

$$T \equiv R\zeta^2/(n-\delta)^2 \tag{48}$$

which, when binomially expanded (assuming $\delta \ll n$)

$$T = R(\zeta/n)^2(1+2\delta/n+\ldots) \tag{49}$$

exhibits this n^{-3} correction. A Rydberg series for which δ is a smooth function of n is referred to as 'unperturbed'. It has been shown (Ritz 1903, Sommerfeld 1919, 1920, Hartree 1928) that the dependence upon principal quantum number is given by the Ritz expansion

$$\delta = b_0 + b_1/(n-\delta)^2 + b_2/(n-\delta)^4+\ldots. \tag{50}$$

When expressed as a series in $1/(n-\delta)$ rather than $1/n$ (cf Edlén 1964, p 123, footnote 2) only even powers occur. For small values of δ this also corresponds to an even power series in $1/n$, which can be understood from the classical model developed here. Ignoring questions of mathematical rigor arising when comparing coefficients of a power series in a variable which does not take on continuous values (Carleman 1922), we compare equations (38), (39), (47) and (49) and associate the Ritz coefficients b_0 and b_1 as

$$b_0 = \frac{\alpha^2\zeta^2}{2}\left(\frac{1}{k}-\frac{3}{4n}-\frac{\langle \boldsymbol{l}\cdot\boldsymbol{s}\rangle}{k^3}\right)+\frac{3\alpha_d\zeta^2}{4a_0^3k^5}+\frac{35\alpha_q\zeta^4}{16a_0^5k^9}+\left(\frac{\zeta_c\rho}{8a_0}\right)^{1/2} \tag{51}$$

$$b_1 = -\frac{\alpha_d\zeta^2}{4a_0^3k^3}-\frac{15\alpha_q\zeta^4}{8a_0^5k^7}+\frac{1}{\pi}\left(\frac{\zeta\rho}{2a_0}\right)^{3/2}. \tag{52}$$

(The quantity involving $3/4n$ in the fine structure is in violation of the n dependence of

equation (49), but it is very small compared to other contributions and can be neglected in this context.) Equations (51) and (52) display a well known empirical fact, namely that the sign of b_1 establishes whether a given state is penetrating or non-penetrating. The polarisation corrections to b_1 are negative, but are generally of smaller magnitude than the positive penetration corrections, and are observed only if penetration is absent.

5. Application—penetration effects for the 3s*n*g G term values in Si III

For ions of the alkali-like Li and Na isoelectronic sequences, it has been found that the term values are well described by the non-penetrating portion T_{non} alone (equation (38)) for all states for which the orbital angular momentum of the active electron exceeds that of any of the passive electrons in the inert-gas core (Edlén 1978, 1979). For the alkaline-earth-like Be and Mg isoelectronic sequences, term values have also been found to be described by T_{non}, but only for much higher angular momentum states, $l \geqslant 5$. An example of this can be seen in figure 1 (Toresson 1960), where the H and I states of Si III are linearly related through equation (41), whereas the G states are not. Since a g orbital is 'non-penetrating' in an alkali-like atom but 'penetrating' in an alkaline-earth-like atom, the deviations from T_{non} for the latter probably arise mainly from interactions with the single out-of-shell s core electron. These deviations could be due not only to electrostatic charge penetration of the s and g orbitals, but also to npn'f and nd^2 configuration interactions, exchange effects and, to a lesser extent, intermediate coupling. The exchange and intermediate coupling effects can be eliminated by formation of an appropriately weighted term value centroid of the singlet and triplet fine-structure states, $\bar{T}$, given by

$$\bar{T} \equiv (T(^1L_l) + T(^3L_l))/2 + (T(^3L_{l+1}) - T(^3L_{l-1}))/2(2l+1). \tag{53}$$

It can easily be seen from the equations for the energy of a two-electron $nsn'l$ system (Edlén 1964, equation (16.1), p 111) that both the electrostatic exchange integral and the spin–orbit integral drop out of equation (53). Thus $\bar{T}$ involves only the electrostatic direct integral, so this is the quantity which is most likely to resemble a classical analogue. Although configuration interaction is not included in the semiclassical approach proposed here, its presence might be expected to manifest itself through irregularities superimposed upon the penetration parametrisation. If configuration interaction effects can be treated in this manner, the alkaline-earth-like g states provide a good first application for a semiclassical penetration parametrisation, since penetration of the single out-of-shell core electron charge cloud should be a much less violent perturbation than that exhibited by more deeply penetrating systems. Therefore we have fitted the measured Si III data to equation (37) for $l \geqslant 4$ by suitable choices of the penetration parameters ρ and ζ_c.

Since it is clear from figure 1 that Si III H terms can be considered as non-penetrating but the G terms cannot, limits for ρ can be established from the perihelions of the corresponding classical orbits. For the G states the perihelion ranges from 4.607 a_0 for 5g to 3.333 a_0 for the series limit. For the H series limit the perihelion distance is 5 a_0. Thus for the classical model $4.607 < \rho/a_0 < 5$. Various values of ρ within this range were used to map the available measured G term values (listed in table 3) into values for ζ_c using equations (38), (39) and table 2. The substitutions of equations (17) and (18) were used for the powers of k, and the values $\alpha_d = 6.858\ a_0^3$ and $\alpha_q = 16.15\ a_0^5$ extracted

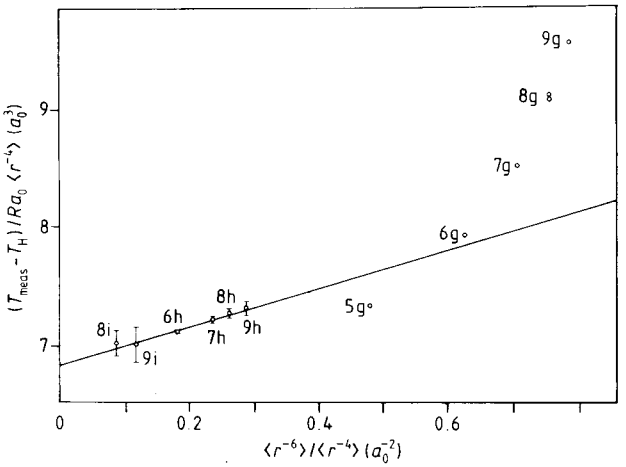

Figure 1. Plot of the variables of equation (41) for the measured G, H and I terms of Si III.

Table 3. 3s*n*g states in Si III.

			$Ra_0(\langle\gamma r^{-s}\rangle-\gamma\langle r^{-s}\rangle)$				
			$s=1$	$s=4$	$s=6$		
n	$\bar{T}_{meas}$	$\bar{T}_{non}$		($\rho=4.7\ a_0$)		$\zeta_c-\zeta$	$\bar{T}_{pred}$
5	39 837.39	39 849.56	66.55	−67.03	−11.68	0.035 00	39 837.55
6	27 665.16	27 662.40	142.19	−116.08	−23.35	0.063 01	27 663.60
7	20 321.31	20 310.57	118.47	−88.73	−19.01	0.080 68	20 322.64
8	15 554.55	15 540.33	93.93	−65.23	−14.48	0.095 15	15 554.81
9	12 285.7	12 271.6	73.5	−48.4	−11.0	0.106 14	12 285.30
10		9 934.8	57.0	−36.6	−8.4	0.113 2[a]	9 946.8
11		8 206.9	44.9	−28.2	−6.6	0.119 1[a]	8 217.1
12		6 893.3	35.8	−22.1	−5.2	0.123 6[a]	6 901.9

[a] Extrapolated

by Toresson (1960) were used so that equation (38) correctly describes the H and I terms. It was found that, although the measured G terms could not all be fitted by a single set of values for ρ and ζ_c, a plot of $\ln(\zeta_c-\zeta)$ versus the orbit eccentricity ε (or, equivalently, the reciprocal of the perihelion distance, which is linearly related to ε) gave very nearly a straight line, as shown in figure 2. It would be difficult to attach a physical significance to this empirical relationship, but it does provide a useful means for extrapolation to higher terms in this Rydberg series. Figure 2 is drawn for $\zeta=4.70$, the value for which the best straight line is obtained.

The results of this parametrisation are listed in table 3. The penetration corrections to $\langle r^{-1}\rangle$ are positive, reflecting the higher attractive Coulomb force in the internal region, whereas the penetration corrections to the polarisation energies are negative, reflecting the assumed disappearance of α_d and α_q in the internal regions. Notice that the internal charges deduced from the measured term values are only very slightly larger than the external charge ($0.03<\zeta_c-\zeta<0.11$ between 5g and 9g). The fact that a slightly different internal charge must be used for each different principal quantum

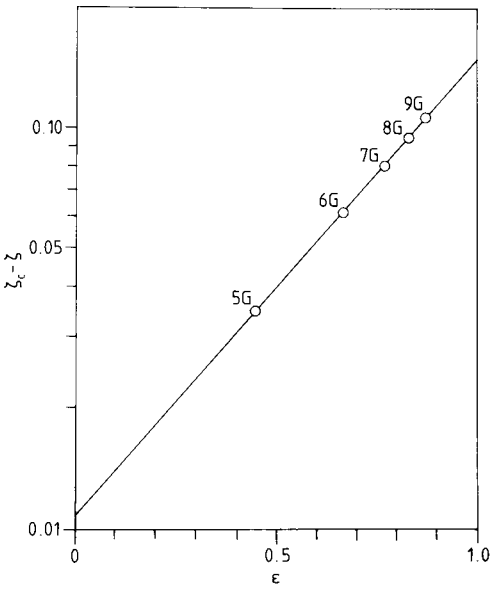

Figure 2. Plot of $\ln(\zeta_c - \zeta)$ against $\varepsilon = [1 - l(l+1)/n^2]^{1/2}$ with $\rho = 4.70\ a_0$ for the measured G terms of Si III.

indicates, of course, that the hollow-core model used here is an oversimplification. However, within the context of this model, the concept of an effective core charge can be empirically useful. The measured data were fitted to a straight line in the mapping space of figure 2, and the corresponding predictions for $\bar{T}$ are listed in table 3. Notice that the measured $n = 6$ and $n = 7$ term values are displaced from the predicted term values in a manner which suggests a repulsive perturbation from some configuration which lies between them. The fit was also used to predict term values for the, as yet unobserved, $n = 10$, 11 and 12 terms. A similar set of predicted term values was obtained using a perturbed Ritz expansion (cf Edlén 1964, equation (23.1), p 137). Although these two approaches were essentially equivalent in their ability to reproduce the measured data, the penetration parametrisation has the advantage of a direct physical interpretation for its fitting parameters which could be useful in extending its application not only along a Rydberg series, but also isoelectronically and homologously.

6. Conclusion

The approach used here has been to represent a many-electron atom by the simplest non-trivial semiclassical model. The simplicity is important, since a full semiclassical treatment, if meaningful, would involve great numerical complexity and offer no advantage over a full quantum mechanical treatment. This approach provides insight into the origin of a number of empirical formulae of atomic spectroscopy and, in appropriate limits, reduces to the core polarisation and Rydberg–Ritz quantum defect parametrisations. The approach also provides a new empirical parametrisation for core polarisation which aids in systemisation of atomic spectral data.

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