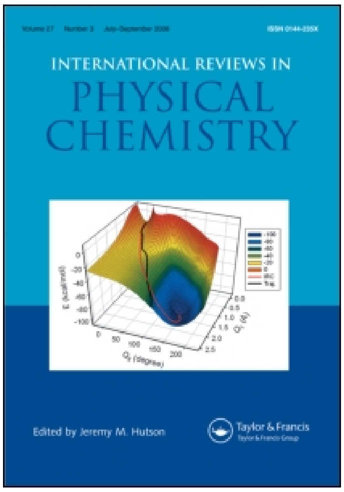
This article was downloaded by:
On: *21 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

The calculation of atomic polarizabilities, with emphasis on the first transition series

G. S. Chandler[a]; R. Glass[a]
[a] Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, Western Australia

To cite this Article Chandler, G. S. and Glass, R.(1986) 'The calculation of atomic polarizabilities, with emphasis on the first transition series', International Reviews in Physical Chemistry, 5: 2, 293 — 300
To link to this Article: DOI: 10.1080/01442358609353394
URL: http://dx.doi.org/10.1080/01442358609353394

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

International Reviews in Physical Chemistry, 1986, Vol. 5, Nos. 2 & 3, 293–300

The calculation of atomic polarizabilities, with emphasis on the first transition series

by G. S. CHANDLER and R. GLASS
Department of Physical and Inorganic Chemistry,
The University of Western Australia, Nedlands, Western Australia 6009

The dipole polarizability gives the first-order effect of an electric field on an electron cloud. Its calculation depends on the perturbation of the wavefunction by the electric field. The application of the variation method to the calculation of polarizabilities is discussed. Emphasis is laid on using configuration interaction wavefunctions in the calculation of transition-metal atom polarizabilities.

Downloaded At: 18:09 21 January 2011

1. Introduction

An atom is distorted by an electric field **E**. A dipole moment arises from this distortion and can be expressed as a power series in the field,

$$\boldsymbol{\mu}=\boldsymbol{\mu}_0+\boldsymbol{\alpha}\cdot\mathbf{E}+\tfrac{1}{2}\boldsymbol{\beta}:\mathbf{E}^2+\tfrac{1}{6}\boldsymbol{\gamma}\vdots\mathbf{E}^3 \tag{1}$$

Here $\boldsymbol{\mu}_0$ is the permanent dipole moment, $\boldsymbol{\alpha}$, a second-rank tensor, is the polarizability and $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ are hyperpolarizabilities. For practical purposes the dipole moment induced by static laboratory fields is adequately described by the polarizability $\boldsymbol{\alpha}$, although hyperpolarizabilities are important in some applications such as determining the induced dipole moment in intense laser radiation fields (Miller and Bederson 1977) and in the Kerr effect (Buckingham and Pople 1955). Higher-order multipole moments are also induced by the field, but will not concern us here.

As the polarizability is the leading term in evaluating the response of an atomic or molecular system it appears in many relations describing the interactions of atoms and molecules with charged particles and involving the interaction of radiation with matter. Consequently important phenomena such as nucleation, catalysis, solvation and the formation of Van der Waal's molecules are connected with the polarizability.

2. Calculation of atomic polarizabilities

The calculation of atomic polarizabilities was reviewed long ago by Dalgarno (1962). All approaches basically depend on the determination of the atomic wavefunction as perturbed in the field.

Consider an isolated atom of nuclear charge Z with N electrons having position vectors $\mathbf{r}_i$. It is convenient to consider the field as being generated by an external charge Z' at position $\mathbf{r}'$, with $|\mathbf{r}'|$ being large compared to $|\mathbf{r}_i|$. The potential energy of the atom in this field is

$$V=\frac{ZZ'}{r'}-Z'\sum_{i=1}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}'|} \tag{2}$$

This may be developed in cartesian coordinates (Buckingham 1959) but in our case it is more straightforward to work in spherical polar coordinates (r_i, θ_i, ϕ_i). The RHS of (2) can be expanded as a sum of Legendre polynomials of order k, $P_k(\cos\theta)$. After the spherically symmetric terms have been dropped this leaves

$$U = -Z' \sum_{i=1}^{N} \sum_{k=1}^{\infty} \frac{r_i^k}{r'^{k+1}} P_k(\cos\theta_i) \tag{3}$$

Denote the wavefunction of the atom in the field as $\psi(\mathbf{r}, r')$. Then, following Dalgarno (1962), the r' dependence of the wavefunction can be included in the following way

$$\psi(\mathbf{r}|r') = \psi_0(\mathbf{r}) + Z' \sum_{k=1}^{\infty} \frac{\psi_1^{(k)}}{r'^{k+1}} + O(Z'^2) \tag{4}$$

provided that the unperturbed state is not degenerate. Normalization of ψ is preserved to the order of Z' by choosing $\psi_1^{(k)}$ so that

$$(\psi_1^{(k)}, \psi_0) = 0 \tag{5}$$

The quantum-mechanical expression for the polarizability can be developed from the first-order wavefunction (4), by substituting it into the expression for the dipole moment associated with wavefunction ψ,

$$\mu = -\left\langle \psi \middle| \sum_{i=1}^{N} r_i P_1(\cos\theta_i) \middle| \psi \right\rangle \tag{6}$$

This substitution yields the following expression for the dipole moment to the order of Z'

$$\mu = -2Z' \sum_{k=1}^{\infty} \frac{1}{r'^{k+1}} \left\langle \psi_1^{(k)} \middle| \sum_{i=1}^{N} r_i P_1(\cos\theta_i) \middle| \psi_0 \right\rangle \tag{7}$$

This is an expansion of μ in terms of the field strength at the nucleus, $E = -Z/r'^2$ and its derivatives. Writing it this way, the leading term is

$$2E\left\langle \psi_1^{(1)} \middle| \sum_{i=1}^{N} r_i P_1(\cos\theta_i) \middle| \psi_0 \right\rangle \tag{8}$$

Comparing (8) with (1) it can be seen that

$$\alpha = 2\left\langle \psi_1^{(1)} \middle| \sum_{i=1}^{N} r_i P_1(\cos\theta_i) \middle| \psi_0 \right\rangle \tag{9}$$

Thus the polarizability is directly related to the first-order dipole correction to the wavefunction, and the calculation of the dipole polarizability resolves into the determination of this correction. Each term in (3) can be treated as a separate perturbing potential, and for the polarizability (9) only the dipole term is needed. Consequently we take

$$V_1 = \sum_{i=1}^{N} r_i P_1(\cos\theta_i) \tag{10}$$

and the perturbed operator as

$$H_0 + EV_1 = H(E) \tag{11}$$

where H_0 is the unperturbed Hamiltonian. The corresponding Schrödinger equation is

$$(H_0 + EV_1)\Psi = \mathscr{E}\psi \tag{12}$$

Downloaded At: 18:09 21 January 2011

Treating the field strength E as a perturbation parameter, the perturbed wavefunction and energy may be expanded as

$$\Psi=\psi_0+E\psi_1^{(1)}+E^2\psi_2^{(1)}+\dots \tag{13}$$

$$\mathscr{E}=\mathscr{E}_0+E\mathscr{E}_1^{(1)}+E^2\mathscr{E}_2^{(1)}+\dots \tag{14}$$

Following the usual development, substitution of (12) and (13) into (11) leads to the series of equations

$$(H-\mathscr{E}_0)\psi_0=0 \tag{15}$$

$$(H-\mathscr{E}_0)\psi_1^{(1)}+(V_1-\mathscr{E}_1^{(1)})\psi_0=0 \tag{16}$$

$$(H-\mathscr{E}_0)\psi_2^{(1)}+(V_1-\mathscr{E}_1^{(1)})\psi_1^{(1)}-\mathscr{E}_2^{(1)}\psi_0=0 \tag{17}$$

In the atomic case $\mathscr{E}_1^{(1)}=0$. Then from (16)

$$\mathscr{E}_2^{(1)}=\langle\psi_1^{(1)}|V_1|\psi_0\rangle \tag{18}$$

From (9) it can be seen (Dalgarno 1962) that the polarizability of the state $|\psi_0\rangle$ can be written in terms of the second-order energy correction,

$$\alpha=-2\mathscr{E}_2^{(1)}=-2\langle\psi_1|V_1|\psi_0\rangle \tag{19}$$

The above outlines the conventional perturbation approach to polarizabilities. However, several recent papers investigate a more general approach (Sadlej 1983) using energy derivatives. The development follows from the expansion of the energy $\mathscr{E}(E)$ in a Taylor series about $E=0$.

$$\mathscr{E}(E)=\mathscr{E}_0+\mathscr{E}\left(\frac{d\mathscr{E}(E)}{dE}\right)_0+\frac{1}{2}\mathscr{E}^2\left(\frac{d^2\mathscr{E}(E)}{dE^2}\right)_0+\dots \tag{20}$$

Comparison of (20) and (14) shows

$$\mathscr{E}_2^{(1)}=\frac{1}{2}\left(\frac{d^2\mathscr{E}(E)}{dE^2}\right)_0 \tag{21}$$

Taking

$$\mathscr{E}(E)=\langle\Psi(E)|H(E)|\Psi(E)\rangle \tag{22}$$

substituting (13) and (11) into the expression and differentiating as in (21) leads to (18) if ψ_0 and $\psi_1^{(1)}$ from (13) obey the Hellmann–Feynman theorem.

Thus a direct use of (19) may involve errors if the unperturbed wavefunction and its first-order correction do not satisfy the Hellmann–Feynman theorem. The difficulty may be obviated by calculating second derivatives or using the finite-field approach (see later).

Expression (19) leads to practical methods for calculating polarizabilities, but before examining them it is useful to develop another expression for the polarizability.

Except in special cases (16) cannot be solved exactly. However, it may be solved formally using the expansion

$$\psi_1^{(1)}=\sum_t{}' a_t^{(1)}\phi_t \tag{23}$$

Downloaded At: 18:09 21 January 2011

where ϕ_t is the eigenfunction of the tth excited state of the unperturbed system, and the prime on the summation indicates that the term $t=0$ is excluded. Then, the second-order energy correction is given by,

$$\mathscr{E}_2 = -\sum' \frac{|\langle\phi_t|V_1|\psi_0\rangle|^2}{\mathscr{E}_t - \mathscr{E}_0} \tag{24}$$

and

$$\alpha = 2\sum_t' \frac{|\langle\phi_t|V_1|\psi_0\rangle|^2}{\mathscr{E}_t - \mathscr{E}_0} \tag{25}$$

Also, since the electric dipole oscillator strength corresponding to the transition from the state $|\psi_0\rangle$ to the state $|\phi_t\rangle$ is defined by

$$f_{0t} = \tfrac{2}{3}(\mathscr{E}_t - \mathscr{E}_0)\left|\left\langle \phi_t \middle| \sum_{i=1}^{N} r_i P_1(\cos\theta_i) \middle| \psi_0 \right\rangle\right| \tag{26}$$

the polarizability of $|\psi_0\rangle$, is given from (21) and (22) by

$$\alpha = \sum_t' f_{0t}/(\mathscr{E}_t - \mathscr{E}_0)^2 \tag{27}$$

Few determinations of polarizabilibities have been made from (27) or (25) because of the contributions from transitions to the continuum. These calculations are referenced by Dalgarno (1962) and in the valuable compilation of polarizabilities by Teachout and Pack (1971).

It is preferable to avoid the complete summation and to make a direct variational attack on the problem. Because polarizabilities are directly related to the change in energy caused by the perturbation they are subject to a variational principle and can be obtained by the usual variation methods. According to Dalgarno (1962), many early studies solved

$$\mathscr{E} = \langle\Psi|H + EV|\Psi\rangle \tag{28}$$

by using a trial wavefunction and minimizing the energy. Recent applications of this method using finite fields in (28) (Cohen and Roothaan 1965), with correlated wavefunctions (Werner and Meyer 1976, Reinsch and Meyer 1976), have calculated the polarizability of the atoms Na through Ca and obtained excellent agreement with the existing experimental values. This method appears capable of great accuracy and has also been recently applied to molecules (Werner and Meyer 1976, Gready *et al.* 1977). One can proceed differently and instead solve (16) for $\psi_1^{(1)}$ and ψ_0 by methods similar to those used in the Hartree–Fock (HF) method. Proceeding in this way yields the coupled Hartree–Fock and uncoupled Hartree–Fock approaches, which have been used in a number of atomic polarizability determinations (Teachout and Pack 1971). However, the SCF methods can give serious errors in polarizabilities because of neglect of correlation effects, as demonstrated by Reinsch and Meyer (1976), Hibbert *et al.* (1977) and Hibbert (1980) for the first and second row of the periodic table.

Another method of attack which the major portion of this paper is devoted to is suggested by the fact that solution of (28) or (16) is equivalent to the simpler problem of minimizing the functional

$$\mathscr{E}_2^{(1)} = \langle\psi_1^{(1)}|H - E_0|\psi_1^{(1)}\rangle + 2\langle\psi_1^{(1)}|V_1|\psi_0\rangle = -\tfrac{1}{2}\alpha \tag{29}$$

Downloaded At: 18:09 21 January 2011

Downloaded At: 18:09 21 January 2011

provided that $|\psi_0\rangle$ is the exact, unperturbed wavefunction (Slater and Kirkwood 1932, Dalgarno and Lewis 1956). Using this variational approach, correlation can be included by expressing both the unperturbed and the perturbed states as a superposition of configurations

$$\psi_0(LS) = \sum_{i=1}^{M} a_i \Phi_i(\alpha_i LS) \tag{30}$$

$$\psi_1^{(1)}(L'S) = \sum_{i=1}^{K} b_i \chi_i(\beta_i L'S) \tag{31}$$

where $\{\Phi_i\}$ and $\{\chi_i\}$ are two sets of single-configuration wavefunctions, and $\{\alpha_i\}$ and $\{\beta_i\}$ define the coupling schemes of the angular momenta of the orbitals. This method was first introduced by Vo Ky Lan *et al.* (1976) because of its usefulness in producing wavefunctions suitable for application to low-energy electron scattering by atoms. Subsequently it has been applied by Hibbert *et al.* (1977) to first-row atoms and by Hibbert (1980) to second-row atoms and ions. We will confine our attention to a discussion of its application to the first transition series.

Because of the nature of the perturbation operator (10) a number of stringent restrictions apply to ψ_1. In relation to ψ_0, ψ_1 must have the same spin, but opposite parity and $|L-L'| \leq 1$, with $L = L' = 0$ not allowed. Since application is confined to atoms, the radial orbitals making up the configurations Φ_i and χ_i are constructed from one-electron Slater functions

$$P_{nl}(r) = \sum_{j=1}^{k} c_{jnl} \phi_{jnl}(r) \tag{32}$$

with

$$\phi_{jnl}(r) = N r^{I_{jnl}} \exp(-\zeta_{jnl} r) \tag{33}$$

where N is the normalizer.

Then, for a particular choice of radial functions, the expansion coefficients $\{a_i\}$ in (30) and the unperturbed energy $\mathscr{E}_0$ are obtained by diagonalizing the unperturbed hamiltonian matrix with a typical element of $\langle \Phi_i | H | \Phi_j \rangle$. The coefficients $\{b_i\}$ in (31) are determined by substituting (33) into (29), taking the inner product with χ_i, and solving the resulting linear equations

$$\sum_{j=1}^{K} (\langle \chi_i | H_0 | \chi_j \rangle - E_0 \delta_{ij}) b_j = -\langle \chi_i | V_1 | \Psi_0 \rangle = d_i \tag{34}$$

The polarizability is then simply given by

$$\alpha = 2 \sum_{j=1}^{K} b_j d_j \tag{35}$$

Ground state HF functions from Clementi and Roetti (1974) are used for the occupied 1s, 2s, 2p, 3p, 3d and 4s orbitals of the transition metals. The pseudo-orbitals have been determined with the following restrictions for the summation in (32), $k = n - l$,

$$I_{1nl} = l + 1$$

and

$$I_{j+1,nl} = I_{jnl} + 1 \tag{36}$$

Thus the coefficients $\{c_{jnl}\}$ in (32) are uniquely determined by the orthonormality requirements of the $\{P_{nl}(r)\}$. Consequently the exponents $\{\zeta_{nl}\}$ are the only variable quantities and can be determined by minimizing the functional (29), which has the effect of optimizing the polarizability α for a particular approximate ψ.

3. Applications

The application of the method can be illustrated by a detailed examination of Sc which has many of the features common to the transition series but avoids potential complications which may arise with a higher occupation of d-orbitals. Recall that use of (29) is formally correct only if $|\psi_0\rangle$ is the exact unperturbed eigenfunction. Truncation is obviously necessary, but it is not clear how far one can go. Hibbert *et al.* (1977) found with first-row atoms that the HF configuration plus the near degeneracy configuration from the $s^2 \rightarrow p^2$ excitation gives average polarizabilities $\bar{\alpha}$ within 10% of those from more elaborate calculations. Table 1 demonstrates this holds also for Sc and presumably for the other early transition elements. In table 1, full CI means all possible single and double excitations from the $3d4s^2$, $3d4p^2$ configurations for ψ_0, and from 3d4s4p for ψ_1. The $1s^2 2s^2 2p^6 3s^2 3p^6$ core is kept frozen. Notice that while omitting all but the leading two configurations causes only a 1% change, omission of the near-degeneracy $3d4p^2$ configuration results in a 43% rise in the polarizability.

It should be borne in mind here that an all singles and doubles CI wavefunction does not formally satisfy the Hellmann–Feynmann theorem (Nebrant *et al.* 1979). However, Gready *et al.* (1977) showed, in the case of Li_2, that finite-field singles and doubles CI wavefunctions closely obey the Hellmann–Feynmann theorem.

If the unperturbed state can be satisfactorily represented by an expansion as simple as a two-configuration function, then it is possible to speak meaningfully about polarizabilities of the electron shells. The conditions that $|L-L'| \leq 1$ translates in the orbital picture into the criterion that most of the polarizability of the shell with angular momentum quantum number l is carried by a polarizing orbital with angular momentum quantum number $l+1$. For the transition elements the major part of the polarizability comes from the 4s shell. This requires a configuration in $\psi^{(1)}$, arising from a single 4s→4p excitation, i.e. in Sc a 3d4s4p configuration, and this is the leading term in each of the allowed $^2P^0$, $^2D^0$ and $^2F^0$ states.

This raises another issue since both the unperturbed and perturbed functions contain important configurations which contain 4p-functions. The orbitals best suited to each of these jobs, correlation in the unperturbed state and polarizability in the perturbed state, are different. The correlating orbitals are more contracted ($\langle r \rangle = 396$ pm in Sc) than the polarizing orbitals ($\langle r \rangle = 738$ pm).

From this it might reasonably be deduced that the 4s-polarizability could only be obtained by optimizing separate correlating and polarizing p-functions. In fact a single

Table 1. Average polarizabilities $\bar{\alpha}$ Å^3 for Sc, with differing ground state functions.†

non-HF orbitals	ψ_0	$\psi_1^{(1)}$	$\bar{\alpha}$
$\overline{4p}\,\overline{4d}\,\overline{4f}$	Full CI	Full CI	23·44
	$3d4s^2, 3d4p^2$	Full CI	23·09
	$3d4s^2$	Full CI	33·63

† From Glass and Chandler (1983).

Downloaded At: 18:09 21 January 2011

Table 2. *m*p functions and the polarizability of Sc in Å^3.

non-HF orbitals	ψ_0	$\psi_1^{(1)}$	$\bar{\alpha}$
4p, $\overline{5p}$	3d4s^2, 3d4p^2 3d4p$\overline{5p}$, 3d$\overline{5p}^2$	3d4s4p, 3d4s5p 3d^{2}4p	15·87
$\overline{4p}$†	3d4s^2, 3d4p^2	3d4s$\overline{4p}$, 3d$^2\overline{4p}$	15·68
$\overline{4p}$‡		3d4s4p, 3d^{2}4p	17·59

† Optimized on 3d4s(^{1}D)4p ^{2}P^0, ^{2}D^0, ^{2}F^0 CSFs in $\psi_1^{(1)}$ (Chandler and Glass 1985).
‡ Optimized on a longer expansion for $\psi_1^{(1)}$ (Glass and Chandler 1983).

p-orbital which fulfils both requirements can be found. The optimization process required is that ψ_0 consists of the single 3d4s^2 HF-configuration and that $\psi_1^{(1)}$ contains only one of the configuration state functions (CSFs) from the possible 3d4s4p couplings for each of the allowed symmetries in the perturbed state (Glass and Chandler 1985 a). Thus, of the two possible couplings in Sc which lead to a ^{2}D^0 state, 3d(^{2}D)4s(^{1}D)4p and 3d(^{2}D)4s(^{3}D)4p, one must be chosen and we have used the first of them. Table 2 compares the result from using a single $\overline{4p}$ function with that from a 4p correlating combined with a $\overline{5p}$ polarizing function. The two results are within 1% of each other. Note that we distinguish between correlating and polarizing orbitals by putting a bar over the latter. Also included in table 2 is the result from a single $\overline{4p}$-function optimized with a larger set of CSFs containing $\overline{4p}$ functions in $\psi_1^{(1)}$. The polarizability is appreciably higher because the resulting p-function is over-balanced in favour of its polarizing function. Other configurations arising from 3d→4p replacements have not been included in $\psi_1^{(1)}$ because they make only a 1% change in the polarizability (Chandler and Glass 1985).

Interestingly, the polarizability of the 4p orbital itself, although not formally occupied in the HF ground-state configuration, makes the next most important contribution to $\bar{\alpha}$, through the 3d4p$\overline{4d}$ configuration. This adds 5·20 Å^3 or *c.* 24% to the total so that in conjunction with the 3d$^2\overline{4p}$ configuration about 28% of the total polarizability comes from the 4p shell.

The 3d shell is not very polarizable and specific optimization of a $\overline{4f}$ orbital to account for it results in only a 1% increase in polarizability (Glass and Chandler 1985 b).

Quite evidently, it is of some interest to know whether use of a single $\overline{4p}$ orbital is adequate for the remaining elements in the first transition series. That it is, is shown in table 3. Zinc stands out as having by far the largest variation with the two approaches. In this respect it is more like calcium than its fellow transition elements.

The superposition of configuration method introduced by Vo Ky Lan *et al.* (1976) for the calculation of polarizabilities appears to be a powerful and, as it leads to short configuration expansions, an economic tool for approaching transition-metal polarizabilities. Not all problems have been discussed here, nor have they been solved yet. For instance similar problems to those faced with the determination of the non-HF p-functions arise for the $\bar{d}$-functions with the increasing importance of 3d^2→nd^2 in excitations in the ground state as one goes across the series. Then there is the question of inter-shell effects arising from excitations from the 3p shell, which Reinsch and Meyer (1976) have shown to be important in K and Ca. Their significance is probably less but, nevertheless, still of some importance in the transition elements. Lastly there is

Downloaded At: 18:09 21 January 2011

Table 3. Polarizabilities (Å^3) from a $\overline{4p}$ function and from the combination of a 4p and $\overline{5p}$ function.

Atom	Polarizabilities with non-HF $\overline{4p}$	 with non-HF 4p + $\overline{5p}$
Sc	15·68	15·87
Ti	13·44	13·61
V	11·80	11·95
Mn	9·53	9·70
Fe	8·53	8·65
Co	7·74	7·75
Ni	7·04	7·14
Zn	6·74	6·06

accuracy. We base our belief in the accuracy of this method on the earlier work for the first and second-row elements which can be compared with some experiments and on the fact that addition of further polarizing functions causes only small changes in the polarizabilities. There is very little in the way of experimental work on the first transition series. The only measurements, to our knowledge, are for Ni and Cu (Liepack and Drechsler 1956) and these probably have large errors associated with them (Miller and Bederson 1977). There is a need for accurate experiments for this group of elements.

Downloaded At: 18:09 21 January 2011

Acknowledgments

Work described in this paper would not have been possible without access to low cost Z-class computing at the Western Australian Regional Computing Centre. The authors gratefully acknowledge this facility.

This work was carried out while R. G. held a University of W.A. Research Fellowship.

References

Buckingham, A. D., 1959, *Quart. Rev.*, **13**, 183.
Buckingham, A. D., and Pople, J. A., 1955, *Proc. phys. Soc.* A, **68**, 905.
Chandler, G. S., and Glass, R., 1985 (to be published).
Clementi, E., and Roetti, C., 1974, *At. Data Nucl. Data Tables*, **14**, 177.
Cohen, H. D., and Roothaan, C. C., J., 1965, *J. chem. Phys.*, **43**, S34.
Dalgarno, A., 1962, *Adv. Phys.*, **11**, 281.
Dalgarno, A., and Lewis, J. T., 1956, *Proc. phys. Soc.* A, **69**, 628.
Glass, R., and Chandler, G. S., 1983, *J. Phys.* B, **16**, 2931.
Glass, R., and Chandler, G. S., 1985a, *J. Phys.* B, **18**, 1307.
Glass, R., and Chandler, G. S., 1985, b, (to be published).
Gready, J. E., Bacskay, G. B., and Hush, N. S., 1977, *Chem. Phys.*, **22**, 141; *ibid.*, **23**, 9.
Hibbert, A., 1980, *J. Phys.* B, **13**, 3725.
Hibbert, A., Le Dourneuf, M., and Vo Ky Lan, 1977, *J. Phys.* B, **10**, 1015.
Liepack, H., and Drechsler, M., 1956, *Naturwissenschaften*, **43**, 52.
Miller, T. M., and Bederson, B., 1977, *Advances in atomic and molecular physics*, Volume 13, edited by D. R. Bates and B. Bederson (New York: Academic Press).
Nebrant, P.-O., Roos, B. O., and Sadlej, A. J., 1979, *Int. J. quant. Chem.*, **15**, 135.
Reinsch, E-A., and Meyer, W., 1976, *Phys. Rev.*, **14**, 915.
Sadlej, A. J., 1983, *Int. J. quant. Chem.*, **23**, 147.
Slater, J. C., and Kirkwood, J. G., 1932, *Phys. Rev.*, **124**, 1431.
Teachout, R. R., and Pack, R. T., 1971, *At. Data*, **3**, 195.
Vo Ky Lan, Le Dourneuf, M., and Burke, P. G., 1976, *J. Phys.* B, **9**, 1065.
Werner, H-J., and Meyer, W., 1976, *Molec. Phys.*, **31**, 855.