

MODEL-POTENTIAL METHODS

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I. Introduction

Many investigators have developed quantitative theoretical methods based on the idea of "core" electrons and "valence" electrons to calculate quantum mechanical properties of many-electron atomic and molecular systems. The terms pseudopotential, model potential and optical potential are used to describe these methods. Although they do have different meanings, authors sometimes ignore the distinctions between the names. The distinction between "core" and "valence" electrons may be a matter of choice; it depends on the desired accuracy of the model. What the methods have in common is that they attempt to accurately describe the correlated motions of the valence electrons and reduce the dimensionality of the original many-electron problem by simplifying the treatment of the valence electron-core electron interactions.

Asymptotically, the leading terms of the valence-core interaction have a simple analytical form and usually can be modelled reliably. At short range, on the other hand, the valence-core interaction is extremely complicated and its nonlocal and energy-dependent nature makes it difficult to approximate in terms of local operators. Nevertheless, it appears that many properties of the system do not depend sensitively on the detailed form of the short-range part of the valence-core interaction, which can be replaced effectively by a local potential. Semi-local (angular-momentum dependent) and nonlocal potentials may be employed for improved accuracy, though the use of nonlocal terms will increase the complexity of the calculation.

Some treatments are *ab initio* in that no experimental data are employed in constructing an effective Hamiltonian for the valence electrons, while others are semi-empirical in that they use experimental data (usually energy levels) to determine parameters that occur in the effective Hamiltonian.

In this chapter, we are concerned with model potentials, though results of pseudopotential approaches will sometimes be mentioned. For our purposes, it is sufficient to classify a pseudopotential as a potential containing a short-range repulsive potential whose purpose is to circumvent core-valence orthogonality requirements, while a model potential, which ignores these requirements, will have valence-electron eigenfunctions corresponding to occupied core states.

Pseudopotential and model-potential methods have been reviewed by Weeks *et al.* (1969), Bardsley (1974), Dalgarno (1975) and Hibbert (1982). A monograph by Szasz (1985) gives an extensive review of pseudopotential theory.

Much of the work to date has been concerned with one- or two-valence electron systems having a spherically symmetric core or cores. The molecular work has, in the main, been limited to diatomics. Because of the success of the methods in producing energy levels, potential energy curves, transition probabilities and scattering cross sections of useful accuracy, the literature in the field is very extensive. We have consequently had to be selective in our choice of material for this review; our bias is towards those aspects of model-potential theory and its applications that have been developed by Alex Dalgarno and his co-workers. We have also attempted to avoid overlap with the previous reviews mentioned above. Unless indicated otherwise, atomic units will be used.

II. Development of Model Potentials

Consider an atomic system consisting of a distinct spherically symmetric core plus a number of outer (valence) electrons. The distinction between core electrons and valence electrons is, of course, somewhat arbitrary; in practice,

we shall limit our considerations to systems in which a very few (usually one or two) electrons are designated as valence. The central idea is to construct an approximate Schrödinger equation for the valence electrons alone and so reduce the computational complexity of the problems of making quantitative predictions of properties and interactions of the original many-electron system. This valence-electron Schrödinger equation will depend on the core through an effective potential V , the model potential for the system, whose asymptotic form we now seek to derive. Our analysis follows closely the method introduced initially in a significant paper by Bottcher and Dalgarno (1974) and later comprehensively extended by Peach (1983).

A. LONG-RANGE ASYMPTOTIC FORM OF THE MODEL POTENTIAL

If the Hamiltonian for the unperturbed core electrons is denoted by H_c then the total (exact) non-relativistic Hamiltonian H for the system may be expressed as

$$H = H_c + T + V_c, \quad (1)$$

where T is the kinetic energy operator for the valence electrons and V_c includes their interaction with the core. Bottcher and Dalgarno (1974) assume the existence of a model potential V whose eigenvalues match the energies E_r of the Rydberg levels,

$$(T + V)\Psi_r = E_r\Psi_r, \quad (2)$$

and construct V by treating $\Delta V = V_c - V$ as a perturbation.

Let Φ_c and \mathcal{E}_c be, respectively, the eigenfunctions and eigenvalues of the core Hamiltonian H_c . We now solve the Schrödinger equation for the system,

$$H\chi = (H_c + T + V + \Delta V)\chi = E_A\chi, \quad (3)$$

by treating $H_0 = H_c + T + V$ as the zero-order operator whose eigenfunctions $\Phi_c\Psi_r$ satisfy

$$H_0(\Phi_c\Psi_r) = (\mathcal{E}_c + E_r)(\Phi_c\Psi_r). \quad (4)$$

We restrict our attention to those solutions of Eq. (3) that correspond in zero-order to states in which the core is in its (spherically symmetric) ground state, denoted by the subscript $c = 0$. Thus, $|E_r|$ will be an ionization potential for the valence electrons.

Introducing the core projection operator, $P = |\Phi_0\rangle\langle\Phi_0|$, and its orthogonal complement, $Q = 1 - P$, allows the Schrödinger Eq. (3) to be written as

$$P(H - E_A)P|\chi\rangle - P\Delta VQ \frac{1}{Q(H - E_A)Q} Q\Delta VP|\chi\rangle = 0. \quad (5)$$

Setting $|\Psi\rangle = \langle\Phi_0|\chi\rangle$ in this equation reduces it to

$$(T + V + U)\Psi = E\Psi, \quad (6)$$

where $E = E_A - \mathcal{E}_0$ and

$$U = \langle\Phi_0|\Delta V|\Phi_0\rangle - \langle\Phi_0|\Delta VQ \frac{1}{Q(H - E_A)Q} Q\Delta V|\Phi_0\rangle. \quad (7)$$

Eq. (6) will be the same as the model Schrödinger Eq. (2) for the valence electrons, provided $U \equiv 0$, a condition that allows an expression for the model potential V to be developed. This may be achieved by making the formal expansion

$$\frac{1}{Q(H - E_A)Q} = \frac{1}{D + Q\Delta VQ} = \frac{1}{D} - \frac{1}{D} Q\Delta VQ \frac{1}{D} + \dots, \quad (8)$$

where $D = Q(H_c + T + V - E_A)Q$. If we now make the fundamental assumption that the core excitation energies, $|\mathcal{E}_0 - \mathcal{E}_c|$, are large compared to valence transition energies, $|E_v - E_r|$, we can further expand $1/D$ as

$$\frac{1}{D} = \frac{1}{Q(H_c - \mathcal{E}_0)Q} \sum_{k=0}^{\infty} \left[Q(E - T - V)Q \frac{1}{Q(H_c - \mathcal{E}_0)Q} \right]^k. \quad (9)$$

Then, retaining only the first two terms on the right-hand side of Eq. (8), the condition $U \equiv 0$ results in

$$V = V_0^{(1)} + \sum_{k=0}^{\infty} V_k^{(2)} + \sum_{k=0}^{\infty} \sum_{k'=0}^{\infty} V_{kk'}^{(3)}, \quad (10)$$

where

$$V_0^{(1)} = \langle\Phi_0|V_c|\Phi_0\rangle, \quad (11)$$

$$V_k^{(2)} = -\langle\Phi_0|V_c G_c [(E - T - V)G_c]^k V_c|\Phi_0\rangle \quad (12)$$

and

$$V_{kk'}^{(3)} = \langle\Phi_0|V_c G_c [(E - T - V)G_c]^k \Delta V G_c [(E - T - V)G_c]^{k'} V_c|\Phi_0\rangle. \quad (13)$$

In Eq. (12) and Eq. (13), G_c is the Green's function for the unperturbed core defined by

$$G_c = \sum_{c \neq 0} |\Phi_c\rangle \frac{1}{\mathcal{E}_c - \mathcal{E}_0} \langle\Phi_c|. \quad (14)$$

For an atomic system consisting of N_c core electrons and N_v valence electrons, the potential V_c is given by

$$V_c = \sum_{i=1}^{N_c} \sum_{j=1}^{N_v} \frac{1}{r_{ij}} - \sum_{j=1}^{N_v} \frac{Z}{r_j} + \sum_{j=1}^{N_v} \sum_{j' > j}^{N_v} \frac{1}{r_{jj'}}, \quad (15)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and \mathbf{r}_i and \mathbf{r}_j denote, respectively, the position vectors of core and valence electrons relative to the nucleus of charge Z . The long-range forms of the terms in the potential V , Eqs. (10)–(13), may be obtained by employing the conventional multipole expansion of V_c in terms of spherical harmonics and making the assumption that $r_i < r_j$. It is easy then to show that

$$V_0^{(1)} = - \sum_{j=1}^{N_v} \frac{Z - N_c}{r_j} + \sum_{j=1}^{N_v} \sum_{j' > j}^{N_v} \frac{1}{r_{jj'}} \quad (16)$$

$$V_0^{(2)} = - \frac{1}{2} \sum_{j=1}^{N_v} \sum_{j'=1}^{N_v} \sum_{\lambda=1}^{\infty} \alpha^{(\lambda)} \frac{P_{\lambda}(\hat{\mathbf{r}}_j \cdot \hat{\mathbf{r}}_{j'})}{(r_j r_{j'})^{\lambda+1}}, \quad (17)$$

where $\alpha^{(\lambda)}$ is the static 2^λ -pole polarizability of the core (Dalgarno, 1962).

The term $V_1^{(2)}$ in Eq. (12) is the first non-adiabatic correction to V . It can be written as

$$V_1^{(2)} = \frac{1}{2} \sum_{\lambda=1}^{\infty} (\lambda + 1)(2\lambda + 1) \beta^{(\lambda)} \sum_{j=1}^{N_v} \frac{1}{r_j^{2\lambda+4}}, \quad (18)$$

where $\beta^{(\lambda)}$ is a dynamic 2^λ -pole polarizability of the core. The derivation of Eq. (18) has been described in detail by Peach (1983) and subsequently discussed by Norcross (1983).

A second non-adiabatic correction to V is given by the term $V_2^{(2)}$ in Eq. (12), and it may be approximately evaluated to give (Peach, 1983)

$$V_2^{(2)} = 4 \sum_{\lambda=1}^{\infty} (\lambda + 1) \gamma^{(\lambda)} \sum_{j=1}^{N_v} \sum_{j'=1}^{N_v} \frac{P_{\lambda}(\hat{\mathbf{r}}_j \cdot \hat{\mathbf{r}}_{j'})}{r_j^{\lambda+3} r_{j'}^{\lambda+1}} \times \left[(\lambda + 2) E_j + (\lambda + \frac{5}{2}) \frac{Z_j}{r_j} + O(r_j^{-2}) \right], \quad (19)$$

where $\gamma^{(\lambda)}$ is a dynamical correction to $\alpha^{(\lambda)}$. $V_2^{(2)}$ is energy dependent; for the case $N_v = 1$, $E_j = E$ and $Z_j = Z - N_c$, but for $N_v > 1$, E_j and Z_j cannot be given rigorous definitions, though they appear to be related to detachment energies and an effective core charge for the valence electrons.

The third-order static contribution $V_{00}^{(3)}$ to V has been evaluated approximately by Peach (1983) to yield

$$V_{00}^{(3)} = \sum_{j=1}^{N_v} \sum_{j'=1}^{N_v} \left\{ (3 - 2\delta_{jj'}) \left[2\varepsilon(2, 1, 1) \frac{P_1(\hat{\mathbf{r}}_j \cdot \hat{\mathbf{r}}_{j'})}{r_j^5 r_{j'}^2} + \varepsilon(1, 2, 1) \frac{P_2(\hat{\mathbf{r}}_j \cdot \hat{\mathbf{r}}_{j'})}{r_j^4 r_{j'}^3} \right] + O(r_j^{-8}) \right\}, \quad (20)$$

where $\varepsilon(2, 1, 1)$ and $\varepsilon(1, 2, 1)$ are hyperpolarizabilities for the atomic core.

For a one-electron system we have, with an obvious change of notation,

$$V = -\frac{Z - N_c}{r} - \frac{\alpha_d}{2r^4} - \frac{\alpha_q - 6\beta_1 - 48\gamma_1 E}{2r^6} + \frac{28(Z - N_c)\gamma_1 + 2\epsilon(2, 1, 1) + \epsilon(1, 2, 1)}{r^7} + O(r^{-8}), \quad (21)$$

while for a two-electron system, neglecting energy-dependent terms and terms that decay more rapidly than r^{-6} ,

$$V = \frac{1}{r_{12}} - (Z - N_c)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) - \frac{\alpha_d}{2}\left(\frac{1}{r_1^4} + \frac{1}{r_2^4}\right) - \frac{\alpha_q - 6\beta_1}{2}\left(\frac{1}{r_1^6} + \frac{1}{r_2^6}\right) - \frac{\alpha_d}{r_1^2 r_2^2} P_1(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2). \quad (22)$$

The last term on the right-hand side of Eq. (22) is the "dielectric" term (Chisholm and Öpik, 1964).

B. CORRECTED FORMS OF THE MODEL POTENTIAL

In the previous section, we presented the long-range form of the interaction of the outer valence electrons with the tightly bound core electrons. In practice, it is necessary to modify the potential V to attempt to give a more realistic description of the short-range interactions, which include exchange forces. Several modifications may be introduced. First, because all the terms in the multipole expansion for the long-range potential V are strongly singular at the origin, it is necessary to introduce cut-off functions $W_n(r/r_c)$, where r_c is a cut-off parameter usually chosen to be of the order of the core radius. Many different forms of $W_n(x)$ have been employed in applications, e.g., $1 - \exp(-x^n)$, $x^{2n}/(x^2 + 1)^n$, $1 - (1 + x + x^2/2! + \dots + x^n/n!)\exp(-x)$ and $(1 - \exp(-x))^n$. Some authors treat r_c as a variable parameter to be chosen to reproduce accurate experimental data (see, for example, Weisheit and Dalgarno, 1971a; Norcross, 1973; and Norcross and Seaton, 1976).

A second modification to V is to replace the monopole term in $V_0^{(1)}$, Eq. (16), by a more realistic core potential, possibly including nonlocal exchange terms. One possibility is to evaluate Eq. (11) for $V_0^{(1)}$, with Φ_0 the Hartree-Fock isolated core wave function (Bottcher and Dalgarno, 1974). Other forms have been used (see, for example, Bardsley, 1974; Norcross and Seaton, 1976; Valiron *et al.*, 1979; and Szasz, 1985).

Another modification is to introduce into V additional short-range correction terms that are chosen empirically to accurately reproduce reliable

experimental or theoretical data for the system or its ions. Typical examples are the use of observed term values for a one-electron system to construct a model potential for the corresponding two-electron system, and the use of atomic term values in the construction of molecular model potentials.

It may be pointed out that, because we have not orthogonalised the solutions of Eq. (2) to occupied core states, the lowest solutions of this equation will correspond to occupied core states and therefore will violate the Pauli exclusion principle. In practice, solutions of Eq. (2) are constructed that are orthogonal to core orbitals (Valiron *et al.*, 1979) or to approximate core orbitals (Victor and Laughlin, 1972) and so have an appropriate nodal structure. In a pseudopotential approach (Szasz, 1985), the orthogonality requirement is replaced by a short-range repulsive term in the potential V so that Eq. (2) does not have solutions corresponding to occupied core states, even though the lowest solution is then nodeless.

A question remains concerning the number of terms to retain in the expansion of V in Eq. (10), suitably modified by cut-off functions as described above. As Drachman (1979) has pointed out, the expression on the right-hand side of Eq. (10) is an asymptotic series, not a convergent series, and caution in its use must therefore be exercised. The number of terms that should be retained in principle will often differ from the number which it is possible to include in practice. For example, the values of the polarizabilities $\alpha^{(\lambda)}$, $\beta^{(\lambda)}$, and so forth are not usually well known. In fact, some of these quantities have been treated as parameters and chosen in an empirical manner (Weisheit and Dalgarno, 1971a; Victor and Laughlin, 1972; Norcross, 1973). As a test, consider the simple systems H^- and He , treating them as effective one-electron systems with a spherically symmetric core consisting of a single K -shell electron. For such systems, all terms up to order r^{-7} have been evaluated (Dalgarno, 1962; Seaton and Steenman-Clark, 1977; Drachman, 1979) with the result that

$$V = -\frac{Z-1}{r} - \frac{\alpha_d}{2r^4} W_6\left(\frac{r}{r_c}\right) - \frac{\alpha_q - 6\beta_1}{2r^6} W_8\left(\frac{r}{r_c}\right) + \frac{24\gamma_1 E}{r^6} W_8\left(\frac{r}{r_c}\right) + \frac{\delta_1}{r^7} W_9\left(\frac{r}{r_c}\right), \quad (23)$$

where

$$\alpha_d = \frac{9}{2Z^4}, \alpha_q = \frac{15}{Z^6}, \beta_1 = \frac{43}{8Z^6}, \gamma_1 = \frac{319}{48Z^8}, \delta_1 = 28(Z-1)\gamma_1 + \frac{213}{4Z^8}, \quad (24)$$

with Z being the nuclear charge and E the Rydberg electron energy. The cut-off functions $W_n(x)$ in Eq. (23) have the form

$$W_n(x) = 1 - \exp(-x^n). \quad (25)$$

The explicit forms of the model potentials v_M are

$$v_M = -\frac{1}{r} + V_{1s} + X_{1s} + V_k + U_k^{(S)}, \quad (26)$$

where V_{1s} and X_{1s} represent, respectively, the static and exchange interactions of the outer electron with a fixed hydrogen-like 1s core orbital. The subscript k on V_k indicates that the first k terms ($k = 1, 2, 3, 4$ and 5) on the right-hand side of Eq. (23) were retained. The short-range potentials $U_k^{(S)}(r)$ ($S = 0$ for singlet series, $S = 1$ for triplet series), whose analytical forms are $(a_0 + a_1 r + a_2 r^2)e^{-br}$, were chosen to reproduce observed He term values as accurately as possible.

Table I gives results for helium $1skp^3P^0$ scattering phase shifts in various approximations and compares them with accurate variation-perturbation results of Stewart (1979). It can be observed that, for this simple system, the results progressively deteriorate as terms beyond the first three in the expansion of V , Eq. (23), are included and that little improvement is obtained by using V_3 rather than V_2 . All the model potentials, v_M , gave accurate representations of the bound-state spectra (though it is again preferable to omit the energy-dependent and r^{-7} terms) and only information on bound-state spectra was used to construct the various v_M . The model-potential phase shifts become less accurate as the energy increases because the $2s2p^3P^0$ Feshbach resonance, which lies at $k^2 = 2.48$ Ryd. (Stewart, 1979), cannot be included in the current model-potential formalism.

Calculations were performed also for $1skp^1P^0$ scattering phase shifts in H^- and He and a similar pattern of results obtained. Analogous conclusions have

TABLE I
HELIUM ATOM $1skp^3P^0$ SCATTERING PHASE SHIFTS

k^2	t^a					Stewart (1979)
	1	2	3	4	5	
0.0	0.1235	0.2148	0.2146	0.2135	0.2135	
0.2	0.2222	0.2251	0.2246	0.2214	0.2279	0.2243
0.4	0.2283	0.2321	0.2315	0.2259	0.2367	0.2314
0.6	0.2324	0.2368	0.2362	0.2281	0.2434	0.2364
0.8	0.2350	0.2398	0.2392	0.2287	0.2480	0.2397
1.0	0.2366	0.2415	0.2410	0.2283	0.2508	0.2417
1.2	0.2374	0.2428	0.2419	0.2272	0.2526	0.2429
1.4	0.2375	0.2424	0.2421	0.2257	0.2534	0.2434
1.6	0.2372	0.2420	0.2418	0.2240	0.2536	0.2434
1.8	0.2365	0.2413	0.2412	0.2222	0.2533	0.2431
2.0	0.2347	0.2403	0.2403	0.2208	0.2527	0.2427

^a t is the number of terms retained in the potential V of Eq. (23) (see text).

been reached by Drachman (1982) in his study of high $1snl$ Rydberg levels of helium with $l = 3$ and by McEachran and Stauffer (1983a,b) who concluded that only the dipole part of the polarization potential should be used in their calculations on low-energy elastic scattering of electrons from helium, neon and argon. Drachman (1982) also found that short-range effects could be more important than the r^{-7} and r^{-8} terms in the potential.

The same conclusions will not necessarily hold for other (larger) systems. Analogous tests for larger systems, where the model-potential method has much greater utility, would be more difficult to perform due to the lack of relevant accurate data. Eissa and Öpik (1967) and Öpik (1967a) find that dynamical corrections (the β_1 term in Eq. (23)) for alkali and alkali-like systems are generally less than a few percent of the total polarization energy. On the other hand, Vaidyanathan and Shorer (1982) find that dynamical corrections to the adiabatic core-polarization potential change the quantum defects of some highly excited singlet F and G states of calcium by as much as 50%; Vaidyanathan *et al.* (1982) measured $4snf^1F_3 - 4sng^1G_4$ ($n = 23 - 25$) microwave transition frequencies in calcium, which agree with the dynamical model of Vaidyanathan and Shorer (1982) but which differ by a factor of approximately two from their adiabatic core-polarization model. It should be mentioned that an open-shell Ca^+ core is used by Vaidyanathan and Shorer (1982), resulting in relatively large dynamical effects (due to correlations between the Rydberg and 4s valence electrons), much larger than would be anticipated for closed-shell-core systems.

The coefficient β_1 in Eqs. (21) and (22) may be expressed as (Öpik, 1967b; Kleinman *et al.*, 1968)

$$\beta_1 = \frac{1}{2} \sum_{c \neq 0} \frac{f_{0c}}{(\mathcal{E}_c - \mathcal{E}_0)^3}, \quad (27)$$

where f_{0c} is the oscillator strength from the ground state to excited state c of the core. Equation (27) may be used to estimate the value of β_1 . Kleinman *et al.* (1968) give upper and lower bounds for β_1 , e.g., $\beta_1 \leq \frac{1}{2}\alpha_d/\Delta E_c$, where ΔE_c is the excitation energy of the lowest state of the core to which dipole transitions are allowed.

The factor $\alpha_q - 6\beta_1$ is negative for all systems for which accurate data on α_q and β_1 exist. Gallagher *et al.* (1982) deduced a negative value of $\alpha_q - 6\beta_1$ for Ba^+ from their observed ratio frequency resonance transition wavelengths for highly excited ($n \sim 20$) G, H, I and K states of Ba.

C. EFFECTIVE OPERATORS FOR MODEL-POTENTIAL WAVE FUNCTIONS

It first was shown by Bersuker (1957) that the long-range polarization terms in the potential effect a modification to the electric dipole operator in the calculation of transition matrix elements with valence-electron wave

functions. Consider, more generally, a one-electron operator, D , which can be expressed as

$$D = \sum_i d(i) \quad (28)$$

and define

$$D_c = \sum_{i=1}^{N_c} d(i), D_v = \sum_{j=1}^{N_v} d(j). \quad (29)$$

Through first order, solutions of the Schrödinger Eq. (3) for the system may be written as

$$\chi_1 = (1 + G_c V_c) \Phi_0 \Psi_{v_1}, \chi_2 = (1 + G_c V_c) \Phi_0 \Psi_{v_2}. \quad (30)$$

The matrix element of D , also through first order, is

$$\langle \chi_1 | D | \chi_2 \rangle = \langle \Phi_0 \Psi_{v_1} | D + V_c G_c D + D G_c V_c | \Phi_0 \Psi_{v_2} \rangle \quad (31)$$

which may be expressed as

$$\langle \chi_1 | D | \chi_2 \rangle = \langle \Psi_{v_1} | \tilde{D}_v | \Psi_{v_2} \rangle \quad (32)$$

if \tilde{D}_v is defined as (Bottcher and Dalgarno, 1974)

$$\tilde{D}_v = D_v + \langle \Phi_0 | D_c | \Phi_0 \rangle + \langle \Phi_0 | V_c G_c D_c + D_c G_c V_c | \Phi_0 \rangle. \quad (33)$$

This operator \tilde{D}_v , correct through first order in ΔV , should be used in model-potential calculations of matrix elements of the operator D . An interesting and relevant case is when D is the multipole operator, so that $d(i) = r_i^\lambda P_\lambda(\hat{\mathbf{r}}_i)$. Eq. (33) then provides

$$\tilde{D}_v = \sum_{j=1}^{N_v} \left(r_j^\lambda - \frac{\alpha^{(\lambda)}}{r_j^{\lambda+1}} \right) P_\lambda(\hat{\mathbf{r}}_j), \quad (34)$$

where $\alpha^{(\lambda)}$ is again the 2^λ -pole static polarizability of the core.

For the particular case of the dipole operator ($\lambda = 1$), the derivations by Bersuker (1957) and Hameed *et al.* (1968) give $\alpha^{(1)}(\omega)$, rather than $\alpha^{(1)}$, in Eq. (34), where $\alpha^{(1)}(\omega)$ is the polarizability of the core at the transition frequency, $\omega = |E_{v_1} - E_{v_2}|$. The value of $\alpha^{(1)}(\omega)$ usually is not available; therefore, in practice, $\alpha^{(1)}$ is used. The two values will not differ appreciably for systems in which the core excitation energies are large compared to valence transition energies (Hameed *et al.*, 1968), which is the basis of the model-potential development. Mohan and Hibbert (1987) point out that this assumption is not valid for mercury if it is treated as a two-electron system.

In actual calculations, the polarization term in Eq. (34) needs to be cut off for small values of r_j . For the dipole operator, Weisheit and Dalgarno (1971b) found that amongst the class of cut-off functions $W_n(x) = 1 - \exp(-x^n)$, $W_3(x)$ was the most satisfactory.

III. Applications of Model Potentials

There have been many applications of model-potential methods in atomic and molecular processes. Some of the first applications were concerned mainly with the prediction of energy-level spectra and molecular potential energy curves, but other properties were soon investigated. Currently, the method is used widely in calculations of both bound-state and continuum-state properties of both atomic and molecular systems. We now review a limited selection of some of the applications.

For one-electron atomic systems, we denote the model potential by v_M , which will contain some of the long-range polarization interactions of Eq. (23) as well as short-range local (and in some cases nonlocal) terms (cf. Eq. (26)). The two-electron equation can then be written in the general form (cf. Eq. (22))

$$[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + v_M(1) + v_M(2) + V(12)]\Psi = E\Psi, \quad (35)$$

where $V(12)$ should contain the dielectric term in addition to the Coulombic repulsion $1/r_{12}$.

A. ATOMIC ENERGY LEVELS

A useful application of the method is provided by two-valence-electron systems, to which we restrict the discussion in this section. Chisholm and Öpik (1964) performed calculations on the $4s^2\ ^1S$, $4p^2\ ^1S$ and $3d^2\ ^1S$ states of atomic calcium using a model potential in the form of Eq. (35), including the dielectric term. Similar procedures, but excluding the dielectric term, are adopted by Friedrich and Trefftz (1969). Later, Victor *et al.* (1976a) also used an approach based on Eq. (35) in their studies of calcium. Several authors (Laughlin and Victor, 1973; Norcross and Seaton, 1976; Laughlin *et al.*, 1978; Müller *et al.*, 1984) have reported model-potential calculations on beryllium, and many other two-electron atomic and ionic systems have been investigated also.

The main differences in the various approaches are in the one-electron model-potential terms $v_M(1)$ and $v_M(2)$ in Eq. (35) and in the numerical techniques used to solve the two-electron Schrödinger equation. Thus, Norcross (1973, 1974) uses an l -dependent potential $v_M(r)$ of the form

$$v_M(r) = v(\lambda, r) + v_p(r_c, r), \quad (36)$$

where $v(\lambda, r)$ is a scaled Thomas-Fermi statistical potential (Eissner and Nussbaumer, 1969) and v_p is a polarization potential. The scaling parameter, λ , and the cut-off radius r_c in $v_p(r_c, r)$ are determined empirically to give

agreement between calculated and experimental energies. In practice, different values of λ and r_c are required for each angular momentum l of the valence electron. Norcross and Seaton (1976) use an l -dependent potential given by

$$v_M(r) = v_{\text{HF}} + v_p(r_c, r), \quad (37)$$

where v_{HF} is a Hartree-Fock potential for the core, including the exchange interaction, derived from scaled Thomas-Fermi statistical potential orbitals. Victor and Laughlin (1972) and Laughlin and Victor (1973), on the other hand, employ a local l -independent potential $v_M(r)$ based on a Hartree-Fock core potential and including, as well as long-range polarization terms, an additional short-range correction term $u(r)$ chosen by a least-squares procedure to fit observed one-electron spectra. Laughlin (1983) has modified this approach by using a nonlocal potential, v_M , to simulate the exchange interaction with the core. In Table II, we demonstrate the differences between the energy levels for lithium obtained from a local (V_{loc}) and a nonlocal (V_{ex}) potential for the Li^+ core. The Hartree-Fock $1s$ orbital for Li^+ (Roothaan *et al.*, 1960) is used to construct V_{loc} and V_{ex} . The additional short-range correction terms referred to above in V_{loc} and V_{ex} are, respectively,

$$u_{\text{loc}} = (-3.247 - 0.111r)\exp(-3.58r) \quad (38)$$

$$u_{\text{ex}} = (0.0147 + 0.0005r)\exp(-1.97r). \quad (39)$$

Note that the errors in the eigenvalues of V_{loc} are substantially larger than the errors arising from V_{ex} , particularly for the lower s and p states, and that u_{ex} is a much smaller correction than u_{loc} . From a computational point of view, it is desirable to use local potentials but, due to the difficulty of modelling a nonlocal operator by a local one, higher accuracy is achieved with nonlocal potentials.

To solve the model Schrödinger Eq. (35), Norcross (1974) and Norcross and Seaton (1976) expand Ψ in terms of products of one-electron eigenfunctions of v_M and channel functions, and solve the coupled differential equations for the channel functions numerically. An alternative procedure (Victor and Laughlin, 1972) is a configuration-interaction expansion for Ψ in a basis of eigenfunctions of v_M . Fairley and Laughlin (1984) have shown that to achieve proper convergence such expansions should include the positive-energy eigenvectors that result when v_M is diagonalized using a discrete basis. These positive-energy solutions adequately simulate the continuum eigenfunctions of v_M , without which the set would not be complete.

Model-potential energies of high accuracy for two-electron systems can be obtained, though not of as high accuracy as very refined *ab initio* calculations for small systems. Model-potential methods have the advantage that the computations are relatively straight-forward and inexpensive, even for large systems, and they allow accurate predictions for Rydberg levels.

TABLE II
LITHIUM ATOM ENERGY LEVELS (a.u.)

State	V_{loc}^a	V_{ex}^b	Experiment ^c
2s	-0.19819	-0.19818	-0.19816
3s	-0.07428	-0.07418	-0.07418
4s	-0.03864	-0.03862	-0.03862
5s	-0.02366	-0.02363	-0.02364
2p	-0.13009	-0.13024	-0.13025
3p	-0.05719	-0.05723	-0.05724
4p	-0.03195	-0.03197	-0.03198
5p	-0.02036	-0.02037	-0.02037
3d	-0.05562	-0.05561	-0.05561
4d	-0.03128	-0.03128	-0.03128
5d	-0.02002	-0.02001	-0.02001

^a Calculated with a local model potential (see text).

^b Calculated with a nonlocal model potential (see text).

^c Johansson (1959).

The model-potential approach can provide estimates of the positions and widths of doubly-excited autoionizing resonances. As an example, consider the $3pns\ ^1P^0$ ($n \geq 4$) and $3pnd\ ^1P^0$ ($n \geq 3$) resonances in magnesium, which lie above the $3s^2S$ threshold of Mg^+ and can autoionise to $3skp\ ^1P^0$ continua. Wave functions and energy levels for these resonance states may be calculated, in first order, by omitting the $3s$ orbital from the basis set (in a configuration-interaction expansion) or by orthogonalising the ns channel function (in the coupled differential equations) to the $3s$ orbital. In either case, the result is that the calculated wave functions will be orthogonal to $3skp\ ^1P^0$ continuum functions. A selection of experimental and theoretical results for the positions of these autoionising levels is presented in Table III. There is considerable discrepancy between the experimental energies for the lower members of the $3pns\ ^1P^0$ series, which autoionise rapidly and, consequently, give rise to broad peaks in the observed spectra. The model-potential results of Laughlin and Victor (1973) agree well with those of Mendoza (1981) who followed the method of Norcross and Seaton (1976). The difference between these two sets of results is a measure of the shift caused by interaction of the discrete $^1P^0$ levels with the $3skp\ ^1P^0$ continuum, which was not included by the former authors.

Finally, in this section we demonstrate the high accuracy that may be achieved in model-potential energy-level predictions. Laughlin (1983) and

TABLE III
ENERGIES (eV) OF $^1P^0$ AUTOIONIZING STATES OF MAGNESIUM RELATIVE TO GROUND STATE

Level	Experiment								
	Mehlman- Balloffett and Esteva (1969)	Esteva <i>et al.</i> (1972)	Rassi <i>et al.</i> (1977)	Baig and Connerade (1978)	Martin and Zalubas (1980)	Laughlin and Victor (1973)	Bates and Altick (1973)	Mendoza (1981)	Chang (1986)
3p4s	9.86	9.52	9.81	9.75	9.752	9.62	10.0	9.706	9.655
3p5s	10.93	10.86	10.97	10.92	10.917	10.90	11.1	10.91	10.898
3p6s	11.39	11.35	11.41	11.35	11.385	11.38	11.5	11.38	11.376
3p7s	11.62	11.60	11.64	11.61	11.614	11.60		11.62	11.611
3p3d	10.65	10.65	10.64	10.65	10.653	10.61	10.8	10.66	10.686
3p4d	11.26	11.26	11.26	11.26	11.254	11.25	11.4	11.25	11.276
3p5d	11.55	11.55		11.55	11.549			11.55	11.556
3p6d	11.71	11.70		11.71	11.706			11.71	11.712

TABLE IV
TRANSITION WAVELENGTHS (nm) IN THE QUARTET SPECTRUM OF BE II

Transition	Theory			Experiment	
	Galán and Bunge (1981)	Froese- Fischer (1982)	Laughlin (1983)	Mannervik <i>et al.</i> (1981)	Bentzen <i>et al.</i> (1981)
2p3d $^4D^0$ -2p4f 4F	437.18	437.8	442.5	437.11	
2s3d 4D -2s4f $^4F^0$	433.01	433.2	434.9	432.96	
2s3d 4D -2p3d $^4F^0$	351.08	349.9	351.4	351.05	
2s4f $^4F^0$ -2p4f 4F	340.60	341.4	341.3	340.54	
2s3d 4D -2p3d $^4D^0$	338.06	337.94	337.94	337.99	
2s2p $^4P^0$ -2p 2 4P		233.1	229.54	232.46	
-2s3d 4D		86.79	86.82		86.71
-2s4s 4S		75.52	75.64		75.44
-2p3p 4P		71.38	71.44		71.42

Fairley and Laughlin (1984, 1985, 1987) have applied a model-potential method to the $1s2snl$ and $1s2pnl$ quartet levels of the lithium sequence, systems that provide the simplest possible applications for a two-electron model potential. The one-electron potentials used not only reproduce observed $1snl^3L$ term values to within experimental uncertainty, but also satisfy the more stringent test of reproducing the highly accurate triplet oscillator strengths of Schiff *et al.* (1971).

Transition wavelengths in the quartet spectrum of Be II are presented in Table IV where they are compared with extensive *ab initio* configuration-interaction calculations (Galán and Bunge, 1981), multi configuration Hartree-Fock calculations (Froese Fischer, 1982) and available beam-foil spectroscopy results. The model-potential wavelengths, though not as accurate as those of Galán and Bunge (1981), compare very favourably with the multiconfiguration Hartree-Fock values. With the help of calculated transition probabilities, several problems in experimental assignments were resolved and some unidentified spectral lines were assigned (Laughlin 1982a,b, 1983; Fairley and Laughlin 1985).

B. OSCILLATOR STRENGTHS AND LIFETIMES

Despite their success in predicting the quartet spectra of lithium-like ions, model-potential wavelengths usually do not approach spectroscopic accuracy. Oscillator strengths are, in practice, much more difficult to calculate than

TABLE V

COMPARISON OF MODEL-POTENTIAL OSCILLATOR STRENGTHS WITH OTHER VALUES

System	Transition	Oscillator strength	
		Model potential	Other
Li II	1s2s 3S -1s2p $^3P^0$	0.3083 ^a	0.3079 ^b
Li II	1s2p $^3P^0$ -1s3d 3D	0.6241 ^a	0.6243 ^c
Be III	1s2s 3S -1s2p $^3P^0$	0.2137 ^d	0.2131 ^b
Be III	1s3s 3S -1s3p $^3P^0$	0.3563 ^d	0.3557 ^b
Be II	1s2p ² 4P -1s2p3d $^4D^0$	0.619 ^d	0.611 ^e , 0.626 ^f
Be I	2s ² 1S -2s2p $^1P^0$	1.372 ^g	1.344 ^h , 1.38 \pm 0.12 ⁱ , 1.341 \pm 0.047 ^j
C III	2s ² 1S -2s2p $^1P^0$	0.764 ^g	0.765 ^h , 0.753 \pm 0.026 ^h , 0.754 \pm 0.014 ^j
O V	2s ² 1S -2s2p $^1P^0$	0.513 ^g	0.515 ^h , 0.47 ⁱ , 0.527 \pm 0.014 ^j
Mg I	3s ² 1S -3s3p $^1P^0$	1.72 ^m	1.75 ^h , 1.83 \pm 0.04 ^h , 1.83 \pm 0.09 ^g
Mg I	3s ² 1S_0 -3s3p $^3P_1^0$	2.11.10 ^{-6g}	(2.1 \pm 0.2).10 ^{-6g} , (2.06 \pm 0.29).10 ^{-6g}
Al II	3s ² 1S_0 -3s3p $^3P_1^0$	1.10.10 ^{-5g}	(1.04 \pm 0.05).10 ^{-5g}
Si III	3s ² 1S_0 -3s3p $^3P_1^0$	2.85.10 ^{-5g}	(2.67 \pm 0.16).10 ^{-5g}
Ca I	4s ² 1S -4s4p $^1P^0$	1.822 ⁿ , 1.76 ⁿ , 1.63 ^x	1.75 \pm 0.08 ^h , 1.79 \pm 0.03 ^x
Cu I	4s $^2S_{1/2}$ -4p $^2P_{1/2}^0$	0.214 ^d	0.22 ^h , 0.215 \pm 0.010 ^c
	-4p $^2P_{3/2}^0$	0.432 ^d	0.43 ^h , 0.41 ^h , 0.431 ^c
Ag I	5s $^2S_{1/2}$ -5p $^2P_{1/2}^0$	0.198 ^d	0.247 ^f , 0.215 ^g , 0.196 ^h
	-5p $^2P_{3/2}^0$	0.413 ^d	0.506 ^f , 0.45 ^g , 0.459 ^h
Cd I	5s ² 1S_0 -5s5p $^1P_1^0$	1.319 ^j	1.42 \pm 0.04 ^j , 1.12 \pm 0.08 ^k , 1.30 \pm 0.1 ^l
	-5s5p $^3P_1^0$	0.00160 ^j	0.00200 \pm 0.00003 ^m
Cs I	6s $^2S_{1/2}$ -6p $^2P_{1/2}^0$	0.340 ⁿ , 0.354 ^p	0.351 ^q
	-6p $^2P_{3/2}^0$	0.707 ⁿ , 0.740 ^p	0.714 ^q
Au I	6s $^2S_{1/2}$ -6p $^2P_{1/2}^0$	0.148 ^d	0.19 ^r , 0.18 ^h
	-6p $^2P_{3/2}^0$	0.339 ^d	0.41 ^r , 0.39 ^h
Hg I	6s ² 1S_0 -6s6p $^1P_1^0$	1.174 ^s , 1.195 ^t	1.21 ^l , 1.15 ^u , 1.18 ^v
	-6s6p $^3P_1^0$	0.0254 ^s , 0.0234 ^t	0.0237 \pm 0.0004 ^w , 0.0249 \pm 0.0004 ^x

^a Fairley and Laughlin (1984)^r Laughlin and Victor (1979)^h Moise (1966)^b Schiff *et al.* (1971)^s Furciattiti *et al.* (1975)^j Migdalek and Baylis (1986)^c Weiss (1967)^t Kwong *et al.* (1982)^k Lurio and Novick (1964)^d Laughlin (1983)^u Johnson (1985)^l Baumann and Smith (1970)^e Galán and Bunge (1981)^v Kwong *et al.* (1983)^m Andersen and Sorensen (1972)^f Froese Fischer (1982)^w Victor *et al.* (1976a)ⁿ Byron *et al.* (1964)^g Laughlin *et al.* (1978)^x Hafner and Schwarz (1978)^o Norcross (1973)^h Sims and Whitten (1973)^y Hansen (1983)^p Weisheit (1972)ⁱ Hontzas *et al.* (1972)^z Kelly and Mathur (1980)^q Fabry and Cussenot (1976)^j Reistad and Martinson (1986)^{aa} Migdalek and Baylis (1978)^h Einfeld *et al.* (1971)^k Reistad *et al.* (1986)^{bb} Lvov (1970)^s Migdalek and Baylis (1985)^l Pinnington *et al.* (1974)^{cc} Hannaford and McDonald (1978)^t Mohan and Hibbert (1987)^m Victor *et al.* (1976b)^{dd} Bell and Tubbs (1970)^u Abjean and Johannin-Gilles (1976)ⁿ Froese Fischer (1975)^{ee} Curtis *et al.* (1976)^v Lurio (1965)^o Kelly and Mathur (1978)^{ff} Penkin and Slavenas (1963)^h Halstead and Reeves (1982)^p Liljeby *et al.* (1980)^{gg} Lawrence *et al.* (1965)^x Mohamed (1983)

energy levels, because they depend on off-diagonal matrix elements of the dipole operator. Experience suggests that refined model-potential calculations produce very reliable oscillator strengths. Apart from a few extensive calculations on small systems, rather few oscillator strengths are known with high precision, nor are there many precise measurements. We assemble in Table V some model-potential predictions and compare them with other accurate data to give substance to our claim that model-potential oscillator strengths are reliable.

The relative size of the correction arising from the dipole term in the modified dipole operator (cf. Eq. (34)) is of some interest. A trivial observation is that the magnitude of the correction is proportional to the dipole polarizability of the core, and so it will play an increasingly important role as the number of core electrons increases. A correction of approximately 1% is obtained by Caves and Dalgarno (1972) for the oscillator strength of the 2s-2p resonance transition in lithium ($\alpha_d = 0.1923$), whereas a correction of approximately 15% is calculated by Norcross (1973) for 6s-6p transitions in cesium ($\alpha_d = 19.06$).

It also is clear that the relative size of the correction will depend on the magnitude of the unmodified value, so that for weak transitions that, due to cancellation, have small dipole matrix elements, the modification to the dipole operator may become very important. In fact, factors of two or more have been found for some weak transitions (Weisheit and Dalgarno 1971b; Butler *et al.* 1984).

A somewhat disturbing feature is that the matrix element of the core-polarization correction to the dipole operator may be sensitive to the cut-off radius r_c (Weisheit, 1972; Laplanche *et al.*, 1983). Again, this is likely to be important only for weak transitions, but it has also been found to occur in bound-free transitions (photoionization).

Oscillator strengths or, equivalently, transition probabilities, have many important applications, for example, in deducing relative abundances in plasmas from the observed emission. Transition probabilities may be combined to give a radiative lifetime for an excited state. Radiative lifetimes can be measured in the laboratory (e.g., by beam foil or beam gas spectroscopy, laser excitation, Hanle effect, or ion traps), allowing a comparison between theoretical predictions and experimental measurements. Table VI shows such a comparison for core-excited quartet levels of lithium. The experimental measurements here were all carried out using the beam foil technique that has been found to efficiently populate quartet levels of three-electron ions (for a review see, for example, Pinnington, 1985). Some of the earlier measurements are not reliable but there is pleasing agreement between the latest experimental values (Mannervik 1981; Mannervik and Cederquist 1983) and theoretical values. The spectral resolution of the beam foil technique is not high and

TABLE VI
 RADIATIVE LIFETIMES FOR Li I QUARTET LEVELS (ns)

Level	Model potential ^a	Other theory	Experiment
2s3s ⁴ S	6.72	6.72 ^b , 6.9 ^c	7.7 ± 1.0 ^d , 9.7 ± 0.7 ^e
2s4s	16.5		15.4 ± 0.5 ^d , 10.4 ± 2.0 ^f
2s5s	33.2		34 ± 2 ^g
2s3p ⁴ P ^o	150	270 ^h , 140 ^c	
2s4p	276	300 ^h , 300 ^c	
2s5p	399	> 500 ^h	
2p3s	9.25		10.6 ± 0.5 ^d , 11.0 ± 2.0 ⁱ , 11.8 ± 0.2 ^j , 12.4 ± 0.3 ^k
2p ² ⁴ P	5.45	5.76 ^b , 5.78 ^c	5.86 ± 0.15 ^d , 6.4 ± 0.3 ^e , 5.8 ± 0.7 ^j , 6.5 ± 0.3 ^k , 7.0 ± 2.0 ^l
2s3d ⁴ D	4.06	4.15 ^b , 4.22 ^c	4.3 ± 0.1 ^d , 4.5 ± 0.4 ^e , 5.3 ± 1.2 ^j
2s4d	9.59		9.6 ± 0.6 ^d , 5.9 ± 1.0 ^j
2s5d	18.5		17.8 ± 0.6 ^g
2s6d	31.9		26.8 ± 1.6 ^g
2s7d	49.3		44.0 ± 6.0 ^g
2s4f ⁴ F ^o	59.3	60.6 ^b	
2p4f ⁴ F	23.9	23.0 ^b	

^a Fairley and Laughlin (1984); ^b Bunge and Bunge (1978); ^c Weiss (1967); ^d Mannervik (1981); ^e Bickel *et al.* (1969); ^f Berry *et al.* (1972); ^g Mannervik and Cederquist (1983); ^h Bunge (1981); ⁱ Bukow (1981); ^j Gaillard *et al.* (1969); ^k Berry *et al.* (1971); ^l Buchet *et al.* (1969).

the availability of reliable transition probabilities and excited-state lifetimes is a valuable aid in the verification of spectral assignments.

C. PHOTOIONIZATION

Model-potential methods have been widely used in photoionization calculations. Bates (1947) estimated the photoionization cross section of atomic potassium using a one-electron equation for the continuum wave function that included the polarization potential $-\frac{1}{2}\alpha_d/(r^2 + r_c^2)^2$, and adjusted the polarizability α_d of the K⁺ core to try to bring calculated and measured cross sections into agreement. Subsequently, potassium (Weisheit and Dalgarno, 1971a; Weisheit 1972) and other alkali metals (Caves and Dalgarno, 1972; Norcross, 1973; Laughlin, 1978; Butler and Mendoza, 1983) have been studied within the model-potential framework. The nonzero minima in the sodium, potassium, rubidium and cesium cross sections result from the spin-orbit interaction (Seaton, 1951), and ionization of unpolarized alkali atoms by circularly polarized light at wavelengths near the minimum yields highly spin-polarized photoelectrons (Fano, 1969). Weisheit and Dalgarno (1971a) and Weisheit (1972) use precise experimental photoionization data on potassium, rubidium and cesium (Heinzmann *et al.*, 1970; Baum *et al.*, 1972)

to determine values for the effective core radii, r_c , to be used in the dipole operator correction. Norcross (1973), in an extensive investigation of cesium oscillator strengths and ground-state photoionization cross section, used a two-parameter model potential, v_M , of the form given by Eq. (36), to which a spin-orbit potential was added. In this case, the parameters λ and r_c were determined by fitting the 6s, 6p_{1/2} and 6p_{3/2} eigenvalues of $v_M(r)$ to observed term values; different values of r_c are required for the s ($r_c = 3.333$) and p ($r_c = 4.132$) states.

Despite their apparent simplicity and amenability to a model-potential treatment, there has been a perplexing failure in attempts to calculate alkali-metal atom cross sections that agree with experimental measurements. Consider sodium as an example. Results are presented in Fig. 1. All

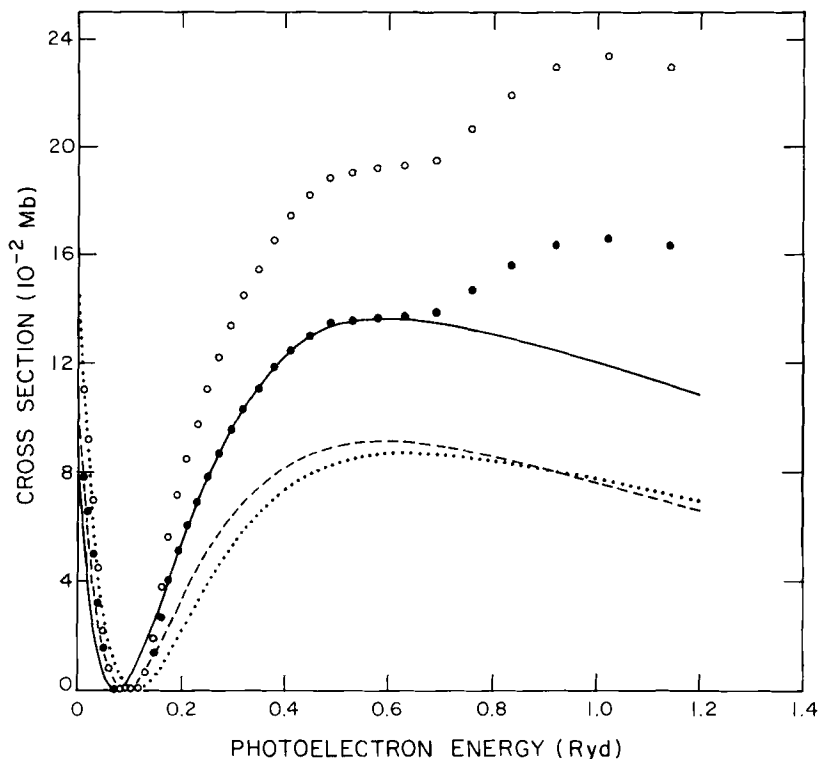


FIG. 1. Photoionization cross section of the ground state of sodium. Open circles: experiment (Hudson and Carter, 1967); full circles: experimental results scaled by a factor of 0.71; full curve: core polarization effects included in both the wave functions and the dipole operator; dotted curve: core polarization effects included in wave functions only; broken curve: core polarization effects omitted. The curves are the theoretical results of Butler and Mendoza (1983), from whom the figure has been adapted. (Reprinted with permission from IOP Publishing Ltd. 1983.)

calculations reproduce the correct qualitative shape of the experimental cross section for a range of energies above threshold, but no calculation provides any evidence for the 'hump' in the experimental value at higher energies. Use of the unmodified dipole operator gives good agreement with experiment near threshold but seriously underestimates the cross section above the minimum. Introducing the core-polarization correction to the dipole matrix element lowers the cross section at threshold but leads to a substantial increase above the minimum. Butler and Mendoza (1983) find that their results agree extremely well with the experimental results of Hudson and Carter (1967) when the latter are scaled by a factor of 0.71. It is of interest to note that the presence of Na_2 dimers, whose cross section is much larger than that of atomic sodium, could increase the cross section significantly (Chang, 1974). In view of the current situation, it is not surprising that there have been repeated suggestions that re-measurement of alkali-atom photoionization cross sections would be extremely valuable.

Ground-state photoionization cross sections for alkali and alkali-like systems are relatively small, rendering them sensitive to minor changes in the wave functions or to perturbations of the dipole operator. It is thus not surprising to find significant differences between the cross sections computed with and without the core-polarization correction to the dipole operator. One would expect some sensitivity to the choice of cut-off radius, r_c , and such behaviour has been noted (Butler *et al.*, 1984).

Photoionization of Rydberg states of alkali-atoms has been considered by Aymar *et al.* (1976, 1984), who used the parametric potential method introduced by Klapisch (1971). This is a one-electron model in which a central potential depending on a number of parameters is determined by minimising the root-mean-square deviation between observed and calculated energies of a selected set of levels. The np and nd cross sections are close to the corresponding cross sections for atomic hydrogen and they can be estimated with reasonable accuracy by use of quantum-defect theory (Burgess and Seaton, 1960).

Finally, in this section we mention very briefly the work of Saraph (1980) who has computed photoionization cross sections (and bound-state oscillator strengths) for several states of O IV. This is an example of a system with a non-closed-shell core and, though it may be viewed as a one-electron model-potential calculation, it is considerably more complex than the applications discussed so far. The six lowest terms ($2s^2\ ^1S$, $2s2p\ ^1,^3P^0$, $2p^2\ ^1S$, 3P , 1D) of O V are used as target functions in a close-coupling calculation of O IV wave functions. The O V wave functions are obtained from the atomic structure code SUPERSTRUCTURE (Eissner *et al.*, 1974) in which the parameters of a statistical Thomas-Fermi potential are varied so as to minimise the energy. Core-polarization terms are not included explicitly in the potential.

D. RELATIVISTIC EFFECTS

It is clear from Sections III.A,B and C that model-potential methods can be applied very successfully to determine the valence structures and properties of light atomic systems. Many workers have studied methods to include relativistic effects in model potentials so that heavier systems could be investigated. Some of these methods include Breit-Pauli operators in a nonrelativistic calculation, while others are based on relativistic Dirac equations.

Semi-empirical model potentials, determined so that they reproduce observed valence energy levels, as discussed in Section II.B, will already include effects of relativity on the core electrons (e.g., relativistic core contraction). Alternatively, the effect of the relativistic contraction of the core electrons may be described by using Dirac-Fock orbitals to generate a core potential. This latter approach was used by Victor and Taylor (1983) in their model-potential calculations on the copper and zinc isoelectronic sequences.

Weisheit and Dalgarno (1971a), in a study of the Cooper minimum in the photoionization cross section of potassium, investigated several forms for a spin-orbit term and adopted

$$V_{\text{SO}} = \frac{1}{2}\alpha^2 \xi(r) \mathbf{l} \cdot \mathbf{s}, \quad (40)$$

where

$$\xi(r) = \frac{(Z - a)}{r^3}, \quad (41)$$

α is the fine-structure constant and a is a screening constant. They find that an average value of $Z - a = 17.33$ reproduces the $n = 4 - 8$ fine-structure splittings to within 3% of the observed values. Norcross (1973) and Theodosiou (1984) employ the parameter-free form

$$V_{\text{SO}} = \frac{1}{2}\alpha^2 \frac{1}{r} \frac{dv_{\text{M}}}{dr} \left[1 + \frac{1}{4}\alpha^2 (\varepsilon_{nlj} - v_{\text{M}}(r)) \right]^{-2} \mathbf{l} \cdot \mathbf{s}, \quad (42)$$

where ε_{nlj} is a valence-orbital energy. This form ensures that $V_{\text{SO}}(r)$ has the correct behavior near the origin.

Laughlin and Victor (1974) and Laughlin *et al.* (1978) use perturbation theory to include the spin-orbit interaction $V_{\text{SO}}(1) + V_{\text{SO}}(2)$, where V_{SO} is given by Eq. (40), and spin-spin and spin-other-orbit interactions, in calculations on two-valence-electron systems. Fine-structure splittings in harmony with observed values are obtained for beryllium and magnesium and calculated intercombination-line oscillator strengths agree well with sophisticated *ab initio* values and with experiment (see Table V).

Ivanov *et al.* (1986) have used a model potential of the form

$$V(r|b) = -\frac{1}{Zr} \left\{ Z - 2[1 - e^{-2r}(1+r)] \right. \\ \left. - (N_c - 2) \left[1 - e^{-br} \left(1 + \frac{3br}{4} + \frac{b^2 r^2}{4} + \frac{b^3 r^3}{16} \right) \right] \right\} \quad (43)$$

in a one-electron Dirac equation, where N_c is the number of core electrons. The parameter b , which is a function of the one-electron quantum numbers n , l , j and the nuclear charge Z , is obtained by making the calculated and measured energies coincide. The values of b thus obtained for several values of Z are fitted to a formula of the type

$$b = b_0 + \frac{b_1}{Z} + \frac{b_2}{Z^2} + \frac{b_3}{Z^3}, \quad (44)$$

which allows interpolation or extrapolation to other nuclear charges. Ivanov *et al.* (1986) present energy level results for $4lj$ and $5lj$ states of the copper isoelectronic sequence for $Z = 36 - 80$. Wavelengths determined using interpolated values of the parameter b agree well with experimental results.

In a recent series of papers, Migdalek and co-workers (Migdalek, 1984; Migdalek and Baylis, 1985, 1986; Migdalek and Bojara, 1987) have carried out calculations of energy levels and oscillator strengths for the mercury and cadmium isoelectronic sequences, treating them as two-electron systems. They use a modified form of the Desclaux (1975) multiconfiguration Dirac Hartree-Fock code, in which a core polarization term

$$V_{CP} = -\frac{1}{2} \alpha_d \left(\sum_{j=1}^{N_v} \mathbf{F}_j \right)^2, \quad (45)$$

where

$$\mathbf{F}_j = \mathbf{r}_j (r_j^2 + r_c^2)^{-3/2}, \quad (46)$$

is added to the Hamiltonian. Note that for $N_v = 2$, V_{CP} includes the dielectric term of Eq. (22). Two choices of the cut-off radius r_c are investigated: firstly, it is taken equal to the mean radius of the outermost core orbital and, secondly, it is adjusted so that the experimental energy of the two-electron system (relative to the core ground state) is recovered. Better agreement with experimental oscillator strengths is achieved with the latter choice.

The transition matrix elements are corrected for core polarization by replacing the dipole operator $\mathbf{D} = \sum_{j=1}^{N_v} \mathbf{r}_j$ by $\mathbf{D} + \mathbf{D}_c$, where

$$\mathbf{D}_c = -\alpha_d \sum_{j=1}^{N_v} \mathbf{r}_j (r_j^2 + r_c^2)^{-3/2}. \quad (47)$$

Since different values of r_c are adopted for the initial and final states, an average value $\mathbf{D}_c = \frac{1}{2}(\mathbf{D}_c^i + \mathbf{D}_c^f)$ is used to calculate the dipole transition matrix elements. It is found that excitation energies and oscillator strengths agree much better with experimental data when core-polarization effects are included. For the higher members of the mercury isoelectronic sequence, the resonance $6^1S_0 - 6^1P_1^0$ oscillator strength results of Migdalek and Baylis (1985) are still about 40% higher than the experimental values. The disagreement is somewhat smaller for the $5^1S_0 - 5^1P_1^0$ transitions in the more highly ionized members of the cadmium sequence (Migdalek and Baylis, 1986). It is possible that these discrepancies may result from difficulties in analysis of the experimental observations.

In earlier calculations on the one-electron copper, silver and gold sequences (Migdalek and Baylis, 1978), the cut-off radius r_c and the dipole polarizability α_d were adjusted to bring the calculated and observed ionization energies into agreement. Again, the oscillator strength results obtained from this model are in much better agreement with the experimental values for the lowest $2S_{1/2} - 2P_{1/2, 3/2}^0$ and $2P_{1/2, 3/2}^0 - 2D_{3/2, 5/2}$ transitions than are the results of calculations that ignore core polarization.

It may be mentioned here that care needs to be taken in the determination of the core cut-off radius, r_c . If, as is often the case, it is chosen empirically to reproduce observed one-electron ionization energies, then the resulting value may be too small. A value of r_c that is too small will clearly overemphasise the role of core polarization in transition matrix elements and the contribution of the dielectric term to the energies of two-valence-electron systems.

For heavy atoms, relativistic effects cause contractions or expansions of the valence orbitals (Desclaux and Kim, 1975). In a calculation on mercury, Mohan and Hibbert (1987) simulate relativistic contraction by adding mass-correction (V_{MC}) and Darwin (V_{Dar}) terms to the model potential v_M for the Hg^{++} core. They use

$$V_{MC}(r) = -\frac{1}{2}\alpha^2[\varepsilon_{nlj} - v_M(r)]^2 \quad (48)$$

and

$$V_{Dar}(r) = -\delta_{l0}\frac{1}{4}\alpha^2\frac{dv_M}{dr}\left(\frac{d}{dr} - \frac{1}{r}\right), \quad (49)$$

where ε_{nlj} is an Hg^{++} orbital energy. The core-polarization terms of Eqs. (45) and (47) used by Migdalek and Baylis (1984) and a spin-orbit operator of the form given by Eq. (40), with $Z - a$ chosen to give the correct $J = 0$ to $J = 2$ fine-structure splittings for $6s6p^3P^0$, are used by Mohan and Hibbert (1987). The calculated oscillator strengths from the ground $6s^2^1S_0$ state to the $6s6p^1P_1^0$ and $6s6p^3P_1^0$ excited states are in reasonably good agreement with those calculated by Migdalek and Baylis (1984) and with the experimental values (see Table V).

A relativistic version of the parametric-potential method of Klapisch (1967) has been developed by Koenig (1972) and Klapisch *et al.* (1977). In this method, the electrons are assumed to move in a central potential $U(r, \mathbf{a})$ depending on a set of parameters, \mathbf{a} , and a zero-order Hamiltonian, which is a sum over one-electron Dirac Hamiltonians, is used. Each parameter describes the radial charge density in a complete shell of the ionic core; the optimal values of the parameters are obtained by minimising the total first-order energies of either the ground level or the ground complex of the spectrum. The method has been employed by Aymar and Luc-Koenig (1977) to study relativistic effects in transition probabilities in the magnesium isoelectronic sequence, and it has been used extensively by Klapisch and co-workers to study the spectra of highly ionized heavy atoms in laser-produced and tokamak plasmas (see, for example, Bauche-Arnoult *et al.* (1985) and Audebert *et al.* (1985)).

A relativistic *R*-matrix approach based on the Breit-Pauli Hamiltonian (Scott and Burke, 1980) was used by Bartschat and Scott (1985a,b) and Bartschat *et al.* (1986) in photoionization studies of mercury and barium. In the barium calculation (Bartschat *et al.*, 1986), a two-electron model, including spin-orbit terms and core-polarization terms of the form $-\frac{1}{2}\alpha_d W_6(r, r_c)/r^4$, where

$$W_6(r, r_c) = \left[1 - \exp\left(\frac{-r}{r_c}\right) \right]^6 \quad (50)$$

is used to generate the initial (ground) and final (continuum) states. The dipole polarizability α_d and *l*-dependent parameter $r_c(l)$ are adjusted to obtain good agreement between calculated and spectroscopic ionization potentials for *LS* states of Ba^+ . The resulting $r_c(l)$ are in the region of 0.6, probably rather small considering that the mean radius of the outermost orbital of the Ba^{2+} ion is 1.927 (Migdalek and Baylis, 1987). The dielectric term is not included in the model and the effects of core polarization on photoionization cross sections are not discussed. The total ground-state cross section is found to be up to an order of magnitude larger than that measured by Hudson *et al.* (1970), though there would appear to be serious doubts about the calibration of the experimental measurements.

IV. Molecular Model Potentials

Ab initio quantum chemistry calculations represent one of the most computationally intensive areas of scientific research. At a given level of approximation, molecular calculations require substantially more computer

resources than atomic calculations because multicenter integrals are significantly more difficult to evaluate than single-center integrals and many nuclear geometries need to be considered, especially for polyatomic molecules. Consequently, many research groups have explored molecular pseudopotential and model-potential methods. The literature is too extensive to allow a comprehensive review, so we shall be selective and concentrate on small diatomic systems with one or two valence electrons. Thus, we shall omit discussion of some important papers, such as those by Stoll *et al.* (1984) and Hay and Martin (1985), where heavy molecular systems are treated using relativistic pseudopotential theory.

A. FORM OF THE MODEL POTENTIAL FOR TWO-CORE SYSTEMS

Consider a diatomic molecule with two spherically symmetric cores, *A* and *B*. Let *R* be the internuclear separation, and let Z_a and Z_b be, respectively, the excess charges on cores *A* and *B*. The generalisation of the theory given in Section II.A has been presented by Bottcher and Dalgarno (1974) and Peach (1983). The general case in which an arbitrary number of valence electrons interact with the cores *A* and *B* is too complex to present here; for a detailed account we refer the reader to Peach (1983). Instead, we write down the long-range forms of the electron-core and core-core interactions correct to the inverse sixth powers of the various distances for the important one-valence-electron system, viz.

$$V = V_a + V_b + V_{ab} + V_{int}. \quad (51)$$

V_a and V_b are the obvious generalisations of Eq. (21). The core-core interaction V_{ab} is

$$V_{ab} = \frac{Z_a Z_b}{R} - \frac{Z_b^2 \alpha_d^{(A)} + Z_a^2 \alpha_d^{(B)}}{2R^4} - \frac{Z_b^2 \alpha_q^{(A)} + Z_a^2 \alpha_q^{(B)} + 2\varepsilon_2(1, 1)}{2R^6}, \quad (52)$$

where α_d and α_q denote static dipole and quadrupole polarizabilities and $\varepsilon_2(1, 1)$ is the exact Van der Waals coefficient for the interaction of cores *A* and *B* (Dalgarno and Davison, 1966). The three-body term V_{int} is given by

$$V_{int} = Z_b \left[\alpha_d^{(A)} \frac{P_1(\hat{\mathbf{r}}_a \cdot \hat{\mathbf{R}})}{r_a^2 R^2} + \alpha_q^{(A)} \frac{P_2(\hat{\mathbf{r}}_a \cdot \hat{\mathbf{R}})}{r_a^3 R^3} \right] - Z_a \left[\alpha_d^{(B)} \frac{P_1(\hat{\mathbf{r}}_b \cdot \hat{\mathbf{R}})}{r_b^2 R^2} - \alpha_q^{(B)} \frac{P_2(\hat{\mathbf{r}}_b \cdot \hat{\mathbf{R}})}{r_b^3 R^3} \right], \quad (53)$$

where \mathbf{r}_a and \mathbf{r}_b are the positions of the electron relative to the nuclei of the cores *A* and *B*, respectively, and \mathbf{R} is the position of nucleus *B* relative to nucleus *A*.

Many applications have been concerned with a neutral one-valence-electron atom interacting with a neutral core B, in which case $Z_a = 1$ and $Z_b = 0$. The extension to a two-valence-electron molecule is straightforward. For such a system, dielectric terms of the form given in Eq. (22) for both of the cores are present in the interaction.

B. APPLICATIONS OF MOLECULAR MODEL POTENTIALS

Early applications were to one-valence-electron molecules with few-electron spherically symmetric cores. Dalgarno *et al.* (1970) carried out calculations on the $^2\Sigma_g^+$ and $^2\Sigma_u^+$ states of Li_2^+ . Terms up to the inverse fourth power were retained in Eqs. (52) and (53), and the electron- Li^+ -core interactions V_a and V_b were modelled by the potential v_M , where

$$v_M(r) = V_{\text{HF}}(r) - \frac{0.09615}{r^4} \left\{ 1 - \exp \left[- \left(\frac{r}{0.47} \right)^6 \right] \right\} - \frac{0.0078}{r^6} \left\{ 1 - \exp \left[- \left(\frac{r}{0.44} \right)^8 \right] \right\}, \quad (54)$$

with $V_{\text{HF}}(r)$ the static Hartree-Fock potential for Li^+ . The results were in good agreement with pseudopotential calculations by Bardsley (1970) and with *ab initio* calculations by Bardsley (1971). Later, Bottcher and Dalgarno (1975) studied more states of the same system employing a model potential with additional exponential terms $u(r)$, where

$$u(r) = (-2.6664 + 1.2323r) \exp \left(\frac{-r}{0.47} \right). \quad (55)$$

Cut-off functions of the form

$$W_n(x) = 1 - \exp(-x) \sum_{t=1}^n \frac{x^{t-1}}{(t-1)!}, \quad (56)$$

were introduced, chosen to simplify the calculation of molecular integrals, the dipole and quadrupole cut-off parameters now having the common value 0.4.

Bottcher *et al.* (1971) carried out similar calculations for Na_2^+ and obtained the cross section for symmetric resonance charge transfer, which can be expressed as an integral over the difference of the lowest two $^2\Sigma_u^+$ and $^2\Sigma_g^+$ potential energy curves. Using similar methods, Bottcher and Oppenheimer (1972) obtained potential energy curves for the six lowest levels of NaLi^+ and calculated the nonresonant charge transfer cross section.

In a series of short papers, Cerjan (1975), Cerjan *et al.* (1976) and Kirby-

Docken *et al.* (1976) studied the results of model-potential calculations for molecular properties other than the potential energy curves. Core- and valence-electron contributions were compared for various one-electron operators and band oscillator strengths and photodissociation cross sections were obtained for Li_2^+ and Na_2^+ . The existence of the correct nodal structure in the model-potential valence-electron wave function is important for obtaining accurate values of many of the one-electron operators.

Model-potential calculations for Σ , Π and Δ excited states of Na_2^+ and K_2^+ have been presented by Henriët (1985). The dipole terms in V_{int} , Eq. (53), are multiplied by cut-off functions, and the cut-off radii are determined to give good agreement with experimental molecular constants for the ground states. Dipole matrix elements for Σ - Σ , Σ - Π and Π - Π transitions between excited states are evaluated using an effective dipole operator corrected for core-polarization effects (Bottcher and Dalgarno, 1975).

The generalisation of the method to the alkali-metal dimer, Li_2 , was carried out by Watson *et al.* (1977). Care had to be taken to avoid collapse to the unphysical states that dissociate to $1s$ and nl . This was achieved by constructing anti-symmetrized trial functions from products of Li_2^+ eigenfunctions, excluding the lowest two $1s\sigma_g$ and $1s\sigma_u$ eigenfunctions. Radiative lifetimes of the vibrational levels of the $A^1\Sigma_u^+$ and the $B^1\Pi_u$ states of Li_2 have been reported (Watson, 1977; Uzer *et al.*, 1978).

Additional one- and two-valence-electron molecular model-potential calculations were carried out for MgHe^+ and MgHe by Bottcher *et al.* (1975). The potential curves were used to calculate line broadening for $\text{Mg}^+(^2\text{P})$ and $\text{Mg}(^1\text{P}$ and $^3\text{P})$ collisions with helium. Collision-induced transitions between fine-structure levels were calculated in the elastic approximation. Malvern (1978) extended the calculations to include Ca as the alkali earth and neon as the rare gas. Orlikowski and Alexander (1984) used these model potentials to calculate fine-structure transitions using close-coupling methods.

For a correct description of atom-rare-gas interactions, such as H-He and Na-Ne, Valiron *et al.* (1979) demonstrated the need to introduce nonlocal terms in the rare-gas model potential, V_b (Eq. 51), in order to obtain wave functions that are consistent with the Pauli exclusion principle. Their procedure is equivalent to constraining the model-potential wave functions to be orthogonal to the rare-gas orbitals. The orthogonality condition involving the outer rare-gas orbitals is particularly important because virtual bound states associated with the rare-gas potential can lead to spurious molecular curve crossings. Pseudopotential approaches suffer from difficulties originating from the short-range repulsive potential introduced to simulate the orthogonality conditions. It appears to be necessary to use l -dependent pseudopotentials to obtain accurate phase shift results for electron-rare-gas scattering (Valiron *et al.* (1979)).

Bottcher (1973) developed a molecular model-potential method for open-shell cores and applied the method to calculate potential energy curves for HeH^+ and He_2^+ . In this treatment, the open shell has zero orbital angular momentum. Peach (1978) studied the potential curves of excited states of helium interacting with the ground state of helium or neon using similar methods. Some of the potential curves are not in good agreement with the calculations of Guberman and Goddard (1975), even at large internuclear separations. A study of an open-shell-core molecular model-potential method for cores with non-zero orbital angular momentum has been presented by Hennecart and Masnou-Seeuws (1985). The electron-open-shell-core interaction is treated using a method due to Feneuille *et al.* (1970) and the molecular model potential is based on the approach of Valiron *et al.* (1979). Potential curves and scattering cross sections are presented for $\text{Ne}(2p^53s \text{ or } 2p^53p)$ interacting with ground state helium or neon.

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