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MOLECULAR POTENTIALS FOR SYSTEMS WITH ONE OR TWO ACTIVE ELECTRONS

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Résumé - Grâce aux méthodes de pseudo-potentiel et de potentiel modèle, des résultats très précis ont été obtenus pour les propriétés moléculaires des systèmes à un électron actif comme les couples alcalin-gaz rare. Pour traiter les dimères alcalins et leurs cations, il est important de décrire avec précision les effets de polarisation de cœur.

Abstract - Owing to model potential and pseudo-potential methods, very accurate results have been obtained for the molecular properties of systems with one active electron such as alkali rare-gas couples. In order to treat the alkali dimers and their cations, it is important to perform an accurate description of core polarisation effects.

I - INTRODUCTION

Owing to laser techniques, much experimental information is now available concerning the ground and excited states of molecules and the dynamical or optical couplings between those states. In many cases, the molecular energies are known with an accuracy better than 1 cm^{-1} . Such a situation is a challenge for theoreticians.

For many systems, the standard methods of quantum chemistry, using extensive configuration interaction, have succeeded in predicting accurate potential curves. However, it is generally difficult to reach an accuracy comparable to the experimental one. In the particular case of systems with one or two active electrons, model potential and pseudo-potential calculations, in which the effect of the *rapid* core electrons on the motion of the *slow* outer(s) electron(s) is simulated by an effective potential fitted on *accurate atomic data*, sometimes provide an excellent accuracy.

Concerning alkali-rare gas systems, it is seven and five years since a 1 cm^{-1} accuracy has first been obtained in the laser spectroscopy of the ground state of NaNe /1/ and NaAr /2/. In the same period, a similar theoretical accuracy has been reached by model potential calculations /3,4/ using the method developed by Valiron et al. /5/.

Fig. 1 - Model potential calculations for the ground state of NaNe /3/ compared with laser spectroscopy determination /1/ (full line, theory ; square and dotted line, experiment)

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In such a method, the non local effects in the electron-rare gas interaction are represented by an explicit orthogonality condition to the outer orbitals of the rare gas. It has given good results for Ne and for Ar /6/ perturbers. It might not be sufficiently accurate for p wave scattering on an helium perturber. Recent calculations of Pascale /7/ using an l-dependent pseudo-potential for the e-helium interaction have improved the agreement with experiment (see Fig. 2).

Fig. 2 - Normalised emission spectrum of the Na3p state in the presence of He at 400 K. Dashed line, experimental data of York et al /8/, solid line calculations of Pascale /7/, dash-dotted line results of Hanssen et al /4/ using the method described in /5/. (from Ref. /7/)

For the excited states, the accuracy depends upon the estimation of the core-core interaction at small internuclear distances, as we shall discuss later on.

During the last three years, the accuracy in the determination of the well in the ground state of the alkali dimer cations has reached a fraction of a wave number, due to extensive studies of the Rydberg states of the alkali dimers using two-photon techniques (see Ref. /9/ to /16/). Such results have stimulated an intense theoretical activity in the field, and the importance of core polarisation effects for the obtention of high quality results has been stressed /17//18/.

During the same period, the laser spectroscopy of the ground state and of the first excited states of the alkali dimers has reached an accuracy of a few wave numbers (see /19/, /20/ and references therein). The most recent determination for the depth D_e of the ground state of Li_2 /21/ and Na_2 /22/ is $8516.9 \pm 0.4 \text{ cm}^{-1}$ and $6022.6 \pm 1 \text{ cm}^{-1}$ respectively. The theoretical results are on the point of reaching the experimental accuracy : Jeung /23/ obtains a well depth of 6020 cm^{-1} for the Na_2 ground state, while Konowalow and Fish /24/ estimate $D_e = 8501 \text{ cm}^{-1}$ for Li_2 . In both case, the inclusion of core polarisation effects is crucial, and the two treatments are intermediate between *ab initio* and effective potential methods.

My aim is to present some of the results obtained recently, and to discuss how in the next future very accurate results could be obtained for the excited states.

2 - EFFECTIVE POTENTIALS FOR THE ALKALI ATOMS : APPLICATION TO ALKALI-RARE GAS SYSTEMS

The basic idea of model potential and pseudo-potential methods is to treat an alkali-rare gas system by solving a one electron Schrödinger equation in order to describe the motion of the active electron in the field of the two cores A and B at a distance R

Fig. 3 - Coordinate system

We therefore must solve the equation :

$$H \Psi_i^\lambda = [T + V_A(r_A) + V_B(r_B) + V_3(\underline{r}, r_A, r_B)] \Psi_i^\lambda = E_i^\lambda \Psi_i^\lambda \quad (1)$$

In (1) T is the kinetic energy, $V_A(r_A)$ and $V_B(r_B)$ are the effective potentials for the interaction of the electron with the cores A and B respectively, V_3 is a three-body tensorial term which depends upon the angle θ_B and comes from the addition of the two electric dipoles induced in B by A and e^- respectively.

2.1.- Definition of $V_A(r_A)$, effective potential for the alkali atoms

In most cases, $V_A(r_A)$ is a parametric potential fitted to properties of the isolated e-A system. The atomic orbitals of the alkali atom are obtained by solving (2)

$$[T + V_A(r_A)] \Phi_i^m(r_A) = E_i^m \Phi_i^m(r_A) \quad (2)$$

The usual procedure consists in fitting the parameters in V_A so that the calculated energies E_i^m are as close as possible from the experimental ones. In a model potential treatment /25/ $V_A(r_A)$ is attractive and contains virtual core orbitals besides the valence orbitals. The atomic functions Φ_i^m therefore possess the correct number of nodes. In a pseudo-potential treatment /26/, $V_A(r_A)$ is repulsive in the core region, leading to nodeless pseudo-orbitals at small r_A . This is illustrated on Fig. 4

Fig. 4 - Schematic representation of the Na 3s orbital in model and in pseudo-potential calculations.

The first question one could ask is then : which is the *true* potential ? We shall show here below that it is a wrong question.

Indeed, the definition of an effective potential comes from an adiabatic separation between the motion of the rapid (core) electrons and of the slow (valence) electrons. Calling $r_1 \dots r_{Z-1}$ the positions of the core electrons, and r_A the position of the valence electron, we may write /27,28/ the total wavefunction for the ground state of the atom A

$$\chi_0(r_1 \dots r_{Z-1} | r_A) \phi(r_A) \quad (3)$$

In (3) χ_0 is the wavefunction for the motion of the core electrons for a *fixed* position r_A of the valence electron. The adiabatic equation :

$$\left[T + W(r_A) - \frac{1}{r_A} \right] \phi(r_A) = \epsilon \phi(r_A) \quad (4)$$

defines the model potential $W(r_A) - 1/r_A$ and describes the motion of the slow electron in the *mean potential of the core*. The physical ideas involved are therefore close to the Born-Oppenheimer separation in molecular physics. The non adiabatic correction :

$$T(r_A) = -\frac{1}{2} \iint \chi_0(r_1, \dots, r_{Z-1} | r_A) \nabla^2 \chi_0(r_1, \dots, r_{Z-1} | r_A) d\tau \quad (5)$$

is small, and limited to the core region. It has been computed through a variational procedure in the case of the lithium atom /27/.

The best effective potential may therefore be defined so that *outside the core region* the wavefunctions solutions of (2) are as close as possible from the "exact" wavefunctions. The physical ideas are therefore very similar to quantum defect theory. The short range potential is an empirical tool for making sure that a large number of excited state wavefunctions have a correct quantum defect *outside the core*. As in quantum defect theory, $V_A(r_A)$ is independent of the energy of the level considered, but is usually l -dependent.

One way of obtaining a good valence wavefunction is to vary the parameters in the potential so that the calculated atomic energies in (2) are as close as possible from the experimental energies. Botcher and Dalgarno /29/, using a 2nd order perturbation theory, have shown that core polarisation effects should be included in the effective potential. This can be done by introducing in the potential an effective core polarisation operator :

$$V_{pol}(r_A) = -\frac{\alpha_d^A}{2 r_A^4} f\left(\frac{r_A}{r_d}\right) - \frac{\alpha_q^A - 6\beta_d^A}{2 r_A^6} g\left(\frac{r_A}{r_q}\right) \quad (6)$$

In (6), α_d^A and α_q^A are respectively the dipole and quadrupole static polarisabilities of the core, β_d^A being the dynamic dipole polarisability - f and g are cut-off functions necessary to avoid the divergence in the core region, r_d and r_q being cut-off parameters typical of the core dimensions. Two comments should be added:

- 1) The core electrons *being not explicitly included* in the treatment, the properties of the core such as its polarisation appear as an effective operator.
- 2) The behaviour of the system during the short period of time when the electron enters the core region is treated as a "black box". The parameters r_d and r_q must then be fitted on experimental data.

In fact, the calculated energies are not very sensitive to the choice of such parameters /30/. Various authors using a large variety of analytical formulas for the potential, have succeeded in reproducing the optical spectrum of the alkali atoms with a good accuracy /31/.

In contrast, the energy variation of the photoionisation cross-sections of the alkali atoms is very sensitive to the choice of the cut-off parameters /18/. A possible improvement in the determination of the effective potential would consist in fitting directly the experimental photoionisation cross-sections. *The influence of such a choice will be discussed later on.*

2.2 - Definition of $V_B(r_B)$ and of V_3

$V_B(r_B)$ represents the interaction of a free electron with a neutral rare gas and is usually fitted on low energy electron-rare gas scattering data /32/ which at present time are known very accurately. We may use the expression :

$$V_B(r_B) = V_{sr}(r_B) - (\alpha_d^B / 2 r_B^4) h_1(r_B / \rho_d) - (\alpha_q^B / 2 r_B^6) h_2(r_B / \rho_q) \quad (7)$$

in which V_{sr} is a short range term (attractive on repulsive, see § 2.1), α_d^B and

$\alpha_q^B = \alpha_q^B - 6\beta_d^B$ are the polarisabilities of the rare gas, ρ_d and ρ_q cut-off radii typical of the dimensions of the core B. The computed phase-shifts are usually sensitive to the choice of such parameters. Besides, as was said in the introduction, the short range term $V_{sr}(r_B)$ must be non local (5,7). The tensorial term: V_3 , and hence the molecular energies, also depend upon the choice of the cut-off parameters :

$$V_3(R, r_B) = \frac{\alpha_d^B}{r_B^2 R^2} \left(h_1 \left(\frac{r_B}{\rho_d} \right) \right)^{1/2} \cos \theta_B + \frac{\alpha_q^B}{r_B^3 R^3} \left(h_2 \left(\frac{r_B}{\rho_q} \right) \right)^{1/2} P_2(\cos \theta_B) \quad (8)$$

θ_B (see fig. 1) is the angle (R, r_B) . Peach /33/ has shown that the cut-off functions in (8) should be the square root of those involved in (7).

It is important to remark that $V_B(r_B)$ -as well as the sum $V_B(r_B) + V_3(R, r_B)$ - is a short range term compared to the $1/r_A$ behaviour of $V_A(r_A)$. The rare gas B may then be considered as introducing an additional R dependent quantum defect on the alkali atomic wavefunctions. On Fig. 5 and 6 we have represented both the atomic wavefunction $\phi_{6p}^{m=0}(r_A)$ solution of (6) and the molecular wavefunction $\psi_{6p}^{m=0}(r_A, R)$ solution of (1) obtained in model potential calculations for the NaHe and NaNe systems.

Fig. 5 (from Ref. 34) - Solid line : sodium atomic wavefunction $\phi_{6p}^{m=0}(r_A)$ as a function of the distance r_A on the quantization axis. Dashed line : molecular wavefunction $\psi_{6p}^{m=0}(r_A, R = 6.75 r_A/r_A)$ in case of an helium perturber located at 6.75 a.u. of the sodium center.

Fig. 6 - Same as Fig. 5 in case of a Ne perturber.

It is clear from Fig. 5 and 6 that :

- a) the molecular wavefunction is very similar to the atomic one, except in the rare gas region where it is strongly modified due to the orthogonality constraint with the occupied orbitals.
- b) the basis set used in model potential calculations must be flexible enough to deal correctly with the modification of the alkali wavefunction in the region of the rare gas core

2.3 - Results for the ionisation energies : molecular quantum defects

The eigenenergy $E_i^{|\lambda|}$ computed in (1) is the ionisation energy, i.e. the energy of an electron in the field of the two cores A^+ and B at distance R for a molecular state of symmetry λ correlated to an atomic $|n\ell m\rangle = |i\rangle$ state.

From the predictions of the Fermi model /35/ and of the asymptotic methods /36/, it has long been known that the difference between the ionisation energy $E_i^{|\lambda|}(R)$ of a molecular Rydberg state of an alkali rare gas system and the energy E_i^{at} of the corresponding atomic state can be scaled by :

$$E_i^{|\lambda|}(R) - E_i^{at} = a_0(K(R)) |\Phi_i^{m=\lambda}(R)|^2 + a_1(K(R)) |\nabla \Phi_i^{m=\lambda}(R)|^2 + \dots \quad (9)$$

where $|\Phi_i^m(R)|^2$ is the probability density of the atomic wavefunction at the rare gas center, $K(R)$ the local de Broglie wavelength associated to it. The quantities $a_0(k)$ and $a_1(k)$ are respectively proportionnal to the s and p wave phase shifts for the elastic scattering of an electron with a wavenumber k by the rare gas B . Such a formula is valid in a region where $K(R)$ is a slowly varying function of R . We have represented on Fig. 7 the ionisation energies of the $\sigma 4p$ and $\pi 4p$ states of the KHe, KNe and KAr systems.

Fig. 7 - Ionisation energies (see text) of the $\sigma 4p$ and $\pi 4p$ states of KHe (dotted line), KNe (broken line) and KAr (full line) as a function of the internuclear distance R . /6/.

The maxima in the Σ states correspond to maxima in the atomic wavefunction so that the rare gas can be considered as "measuring" the atomic probability density at a given point. The Π ionisation energies are proportionnal to the square of the gradient of the atomic wavefunction, which is a severe check on the accuracy of this wavefunction.

The representation of the rare gas B as an additional R-dependent quantum defect is illustrated on Fig. 8, where we have represented as a function of the internuclear distance R the molecular quantum defects δ_l^1 , with

$$E_i^{(1)}(R) = -\frac{R}{(n_i - \delta_l^1(R))^2} \quad (10)$$

In (10) R is the Rydberg constant and n_i the principal quantum number at infinity. We consider three atomic quantum defects, δ^S , δ^P , and $\delta=0$ for $\ell \geq 2$.

Fig. 8 - Molecular quantum defects for the $4p\sigma$ to $9s\sigma$ states of the NaNe and NaAr molecules. The quantum defects curves δ_0^1 (see text) are contained in the shadowed areas /6/, /37/. The δ^q and δ^r curves are correlated to atomic states with $\ell \geq 2$.

It is clear from Fig. 8 that the molecular quantum defects are fairly n -independent. For the states correlated to atomic states with $\ell \geq 2$, the quantum defect curve splits into two curves, one of which exhibits an avoided crossing with the (δ^P-1) curve. It has then been possible to predict collisionally induced transfers between the Na $((n+1)p)$ and Na nd states. The experimental measurements concerning such transfers /38/ are in excellent agreement with theoretical calculations /34/ in which the computed radial and rotational coupling matrix elements are introduced in the collision problem.

In conclusion, one may say that the accuracy of the ionisation energies is due to the quality of the atomic wavefunctions and to the precision of the electron rare gas elastic phase shifts obtained with the effective potentials. Such an accuracy is possible because the motion of the core electrons is sufficiently rapid to allow the introduction of effective potentials.

2.4 - Results for the molecular energy : problem of the core-core term

The energy $\mathcal{E}_i^{|\lambda|}$ of a molecular $|\lambda\rangle$ state is obtained by adding to the ionisation energy $E_i^{|\lambda|}$ the core-core energy $V_{AB^+}(R)$, i.e. the energy of the ground state of the AB^+ molecular ion for an internuclear distance R .

$$\mathcal{E}_i^{|\lambda|}(R) = E_i^{|\lambda|}(R) + V_{AB^+}(R) \quad (11)$$

$V_{AB^+}(R)$ may be expressed as the sum of a polarisation term and of a short range repulsive term due to the overlap of the asymptotic part of the two core wavefunctions (Obviously, the method is no more valid when the atomic clouds are modified by the interaction of the two cores)

$$V_{AB^+}(R) = \mathcal{V}_o(R) - (\alpha_d^B / 2R^4) - (\alpha_q^B / 2R^6) \quad (12)$$

If the polarisabilities α_d^B and α_q^B of the core B are well known, the quantity $\mathcal{V}_o(R)$ - which is generally fitted to ion-atom scattering data or to mobility measurements - is not known very accurately, so that the 1cm^{-1} accuracy available for the ionisation energies is obtained for the molecular energies only at large distances where $V_{AB^+}(R)$ is limited to the polarisation terms. We have shown on Fig. 1 the excellent agreement which exists between theory and experiment concerning the well in the ground state of the NaNe system at 10 a.u. In contrast (see (9)) the well of the first excited Π state is mainly determined by $V_{AB^+}(R)$ and therefore depends markedly upon the estimation of $\mathcal{V}_o(R)$. This is illustrated on Fig. 9 where we have represented the $\Pi 4p$ curve of KAr for two different choices of $V_{AB^+}(R)$

Fig. 9 - Molecular energy curve $\mathcal{E}_1^{4p}$ (see formula (11) in text) of the $A^2\Pi$ state of KAr/6/, obtained through model potential calculations with two choices for the core-core term. Solid line : $\mathcal{V}_o(R)$ has been taken from Ref. /39/ ; dashed line : $V_{AB^+}(R)$ is taken from Ref. /40/ ; Cross : experimental determination of Düren and Tischer /41/ for $\mathcal{E}_1^{4p}(R)$.

However, the core-core term is common to all molecular curves. It should be valuable, especially when accurate experimental information is available for several $\mathcal{E}_i^{|\lambda|}$ curves from collision or spectroscopy experiments, to fit $V_{AB^+}(R)$ directly on experimental results for the AB system. In the work of Düren's group /42/ parameters in $V_B(r_B)$, $V_3(R, r_B)$ and $V_{AB^+}(R)$ have been fitted so that accurate experimental scattering cross-sections can be reproduced from collision calculations involving the $\mathcal{E}_i^{|\lambda|}(R)$ curves. It should be very interesting to use a similar procedure with the curves $E_i^{|\lambda|}(R)$ computed from (1) while $V_{AB^+}(R)$ depends upon adjustable parameters.

3 - GENERALISATION TO OPEN SHELL CORES : CALCULATIONS FOR HeHe^* , HeNe^* , NeNe^*

The effective potential method has been generalised to open shell cores /46,33,48/. For such systems, several states of the AB^+ molecular ion are involved in the calculation, and humps in the excited curves ($1s_5$ 0^- and 1_u of Ne_2) depend markedly upon the estimation of the core-core interaction /48/. *The accurate estimation of the AB^+ curves is an open problem at present time.*

Fig. 9bis. Hump in the $0^- 1s_5$ potential curve of Ne^+-Ne .

Solid line, dotted line : model potential calculations /48/ for two different estimations of the core-core term

Dashed line : fitted /47/ to scattering experiments

4 - STUDY OF THE ALKALI MOLECULAR IONS

4.1 - Molecular quantum defects

In contrast, when we turn to alkali molecular ions such as Li_2^+ , Na_2^+ , K_2^+ , the problem of the core-core term is less crucial, due to the predominance of the $1/R$ term. Nevertheless, the physical situation differs markedly from the preceding one, as the electron now moves in the field of *two* charged cores. In the alkali rare gas problem, we have shown that an *atomic* wavefunction is modified by a R -dependent quantum defect. In the alkali molecular ion problem, we may consider that the short range non coulombic term in the two potentials V_A and V_B introduces two quantum defects *on the H_2^+ wavefunctions*. Such a situation is illustrated on Fig. 10 where we have represented the R -variation of the effective quantum number $n_i - \delta_i^q(R)$ for the Σ states of the Na_2^+ ion:

Fig. 10 - Variation of the effective quantum number $n_i - \delta_i^q(R)$ (see Eq (10)) as a function of the internuclear distance R for the ground and excited $^2\Sigma$ states of the Na_2^+ molecular ion /18/

Avoided crossings are clearly visible, which would be permitted in the H_2^+ problem. In the Na_2^+ case, the potential departs from a pure coulombic potential in the core region, and the supersymmetry of the H_2^+ problem is broken. *It should be worthwhile to perform on such systems experimental investigations similar to the study of Stark effect on alkali atoms.*

4.2 - Ground state of the alkali dimer-cations : core polarisation effects

Model potential and pseudo potential calculations have been used successfully for many years in order to compute the properties of the ground and excited states of such systems /25,26/. It has long been known that the results are sensitive to the introduction of core polarisation effects. *Ab initio* calculations, taking account approximately of core polarisation, generally overestimate the bond length /43/.

Recent very accurate experimental determinations, obtained through two step ionisation techniques /10-16/ have stimulated new calculations. Limiting the polarisation terms to the dipole terms, one obtains the molecular energies by solving the Schrödinger equation :

$$\left[T + V_A(r_A) + V_B(r_B) + V_3(R, r_A, r_B) - \frac{\alpha_d^A}{R^4} + \frac{1}{R} \right] \Psi_i^\lambda(R, r_A, r_B) = \mathcal{E}_i^\lambda \Psi_i^\lambda(R, r_A, r_B) \quad (13)$$

$V_A(r)$ is the potential defined in § 2.1 and α_d^A the polarisability of the two identical cores. The cross polarisation term is now deduced from (6)

$$V_3(R, r_A, r_B) = (\alpha_d^A / R^3) \left\{ r_A^{-2} \cos(R, r_A) \left[f(r_A/r_d) \right]^{1/2} + r_B^{-2} \cos(R, r_B) \left[f(r_B/r_d) \right]^{1/2} \right\} \quad (14)$$

Because of the importance of the V_3 term, the results depend markedly upon the choice of the cut-off radius r_d . This is illustrated on Fig. 11:

Fig. 11 - Potential curve for the ground state of $Na_2^+ /18/$ in the minimum region for various choices of the cut-off radius r_d . Dashed lines : calculations using (a) $r_d=2$ (b) $r_d=3$ (c) $r_d=3.5$ a.u. Full line : calculations using Weisheit's value $r_d=2.35$ (see text). Circles : experimental results /13/. Squares : experimental results /14/.

The determination of the cut-off appears then as an important problem. The V_{pol} term in V_A (see (6)) depending upon r_d , one possibility is to fit the cut-off radius so that the atomic energies eigenvalues of (2) are as close as possible from experiment. Such a procedure has been used in recent pseudopotential calculations /17/. However, recent work using model potential calculations /18/ has shown that the atomic

energies are not very sensitive to the choice of r_d /44/, introducing some arbitrariness in the method. In contrast, however, the atomic dipole moments /28/ and the photoionisation cross sections /45/ are sensitive to r_d . The value 2.35 a.u. fitted by Weisheit /45/ in order to reproduce the minimum in the photoionisation cross-section leads to a satisfactory potential curve /18/ for the ground state of Na_2^+ (see Fig. 11). The results of /17/ and /18/ are compared to experiment on Table 1. In both cases, we have indicated in italics the values obtained when neglecting the cross polarisation term V_3 in the effective hamiltonian.

TABLE 1
Ground state properties of Li_2^+ Na_2^+ K_2^+

	$D_e(\text{eV})$	$R_e(\text{\AA})$	$w_e(\text{cm}^{-1})$	Method
Li_2^+	1.280	3.127		<i>ab initio</i> /43/
	1.293	3.099	263.5	<i>ab initio</i> + core polarisation /12/
	(1.32)	(3.06)		neglecting V_3
	1.30	3.08	268	including V_3 pseudo pot. /17/
	(1.30)	(3.09)		neglecting V_3
	1.28	3.09	283	including V_3 model pot. /18/
	1.27 $\pm$ 0.02 1.2980 $\pm$ 0.0007 1.2836 $\pm$ 0.0031	3.11 $\pm$ 0.01	262.2 $\pm$ 1.5 260	exp /9 / exp /10/ exp /11/
Na_2^+	(1.02)	(3.28)		neglecting V_3
	0.993	3.59	119	including V_3 pseudo pot. /17/
	(1.02)	(3.55)		neglecting V_3
	0.980	3.60	123	including V_3 model pot. /18/
	0.984 0.986	3.60 $\pm$ 0.04 3.60 $\pm$ 0.05	118 120.8 $\pm$ 0.8	exp /13/ exp /14/
K_2^+	(0.91) *	(4.31)		neglecting V_3
	0.823	4.49	72	including V_3 pseudo pot. /17/
	(0.904)			neglecting V_3
	0.801	4.44	75	including V_3 model pot. /18/
	0.794 (?) 0.789 (?)	4.4 4.60	72.5 73.4 $\pm$ 0.5	exp /15/ exp /16/

In the first two lines of table 1 are reported *ab initio* results for the ground state of Li_2^+ . When core polarisation effects are neglected /43/ the bond length is overestimated. In contrast, *ab initio* calculations corrected for core polarisation /12/ provide a bond length in better agreement with experiment.

The importance of the inclusion of the cross polarisation term V_3 is clear also from table 1 especially for K_2^+ . When the active electron and the core A (resp B) simultaneously polarise the core B (resp A)) the resulting force is the sum of the two polarisation forces and depends upon θ_B (see Fig. 1). When we neglect the term V_3 , we assume that the two forces are collinear so we overestimate the polarisation forces and hence the well depth.

The agreement between theory and experiment is satisfactory when V_3 is included. In the case of the K_2^+ ion, the value of the experimental well depth depends upon the well depth in the ground state of the K_2 molecule, which is not known accurately at present. Nevertheless, the experimental accuracy is not yet reached, and further work including a more precise fitting of the cut-off radius r_d , possibly on atomic photoionisation cross sections, is needed.

5 - TREATMENT OF THE TWO ELECTRON PROBLEM : APPLICATION TO ALKALI DIMERS

Fig. 12 - Coordinate system

In the case of two electrons moving in the field of two alkali cores A and B, it is necessary to treat simultaneously

- a) the interaction of the electrons with the two cores
- b) the bielectronic interaction

It is beyond the scope of the present paper to review all the theoretical work on that subject ; an extensive bibliography is available for Li_2 and Na_2 /19,20/. It seems that four kinds of treatment are possible nowadays, according to the methods used to deal with the two problems in a) and b)

5.1 - Effective operator method with configuration interaction

The method described in §4 for the molecular ions has been extended to two electron systems. The model potential treatment has been generalised by Dalgarno's group /25, 49/ while a pseudo-potential treatment of alkali dimers has been developed first by Bardsley and his coworkers /26,50/, then by Valance et al, who treated the excited states /51/. The total hamiltonian is written :

$$H = h(1) + h(2) + \mathcal{V}(1,2) - V_{AB+}(R) \quad * \quad (15)$$

where $h(j)$ is the one electron operator defined in (13)

$$h(j) = T + V_A(r_{Aj}) + V_B(r_{Bj}) + V_B(R, r_{Ai}, r_{Bi}) + V_{AB+}(R) \quad (16)$$

and describes the motion of the active electron i in the field of the two cores. Core polarisation effects are included and it is clear from the perturbative treatment of Bottcher and Dalgarno /29/ that all the one electron operators must be replaced by effective operators, depending of a cut-off radius typical of the core dimensions. For instance, the dipole moment is modified /28/

$$\tilde{r}_{Ai} \rightarrow \tilde{r}_{Ai} \left(1 - \alpha_d^A \tilde{r}_{Ai}^{-3} \left[\rho \left(\tilde{r}_{Ai}/r_d \right) \right]^{3/2} \right) \quad (17)$$

and the bielectronic interaction must include a dielectric term V_{die}

$$\mathcal{V}(1,2) = \frac{1}{r_{12}} - \frac{\alpha_d^A \cos(\tilde{r}_{A1}, \tilde{r}_{A2})}{r_{A1}^2 r_{A2}^2} \left[\rho \left(\frac{r_{A1}}{r_d} \right) \rho \left(\frac{r_{A2}}{r_d} \right) \right]^{3/2} - \frac{\alpha_d^B \cos(\tilde{r}_{B1}, \tilde{r}_{B2})}{r_{B1}^2 r_{B2}^2} \left[\rho \left(\frac{r_{B1}}{r_d} \right) \rho \left(\frac{r_{B2}}{r_d} \right) \right]^{3/2} \quad (18)$$

The dielectric correction, first introduced by Chisholm and Opik /53/, comes from the non additivity of the two potentials for the polarisation of one core by the two electrons simultaneously, and is a cross polarisation term as V_3 . It has to be included in accurate calculations of the affinity of the alkali atom /54/. The method is simple because the core electrons are not explicitly included : this can be done provided one may neglect the valence excitation energies compared to the core excitation energies /29/. The results depend upon the choice of an arbitrary cut-off radius r_d , which has to be chosen unambiguously.

After solving the Schrödinger equation for the molecular ion problem :

$$h(i) \Psi_a^{\lambda_a} = E_a^{\lambda_a} \Psi_a^{\lambda_a}(R, \tilde{r}_{A1}, \tilde{r}_{B1}) \quad (19)$$

one performs a standard configuration interaction treatment by expanding the total wavefunction on antisymmetrized products of mono-electronic orbitals solutions of (13)

$$\mathcal{P}(1,2) = \sum_{ab} \mathcal{A} \Upsilon_a^{\lambda_a}(1) \Upsilon_b^{\lambda_b}(2) \quad (20)$$

and computing the matrix elements of $\hat{V}(1,2)$.

Such a method has given good results, but in many existing treatments either the cross polarisation term V_3 or the dielectric term V_{die1} is neglected.

5.2 - Effective operator method using correlated orbitals

Recently methods have been proposed which treat the one electron problem as in the preceding case but improve the calculation of the two electron correlation. Preuss' group has developed a sophisticated treatment of core polarisation effects, including V_3 and V_{die1} /52/. A non local pseudopotential is fitted to the experimental valence energy of the isolated atoms, and the two electron problem is solved in the framework of the density functional formalism, the charge density of valence electrons with spin + and - respectively being not necessarily identical. *The interest of such a method is that it has easily been generalised to alkali clusters.*

Another approach /55/ treats the one electron problem as in the preceding case, but improves the calculation of the two electron correlation owing to a generalisation of Pluvinaige's treatment for the helium atom /56,57/. Equation (20) is modified to :

$$\mathcal{P}(1,2) = \sum_{ab} \mathcal{A} \Upsilon_a^{\lambda_a}(1) \Upsilon_b^{\lambda_b}(2) u_k^{\lambda_k}(r_{12}) \quad (21)$$

in which $u_k^{\lambda_k}(r_{12})$ describes the motion of the two electrons interacting through the $1/r_{12}$ potential in the lack of an external field. *Such a method should be valuable for the treatment of the excited states.* It has already given promising results for the ground state of Na_2 and K_2 , using three correlated configurations only, but only future work will tell whether the improvement compared to standard configuration interaction techniques is significant.

5.3 - *Ab initio* treatment

Very sophisticated multiconfiguration treatments have been developed for the alkali dimers, especially by Konowalow and coworkers /58,59/. It seems at present time that *ab initio* methods have converged to their optimal result, which, as first demonstrated by Rosmus and Meyer /60/, systematically overestimates the equilibrium distance for the ground state potential curve due to a neglect of core polarisation effects.

5.4 - *Ab initio* treatment modified for core polarisation effects

The most impressive progress has been realised in the last two years through the introduction of core-valence correlation effects in the *ab initio* treatment. In Toulouse /61,62,23/ the perturbative treatment of /29/ has been reconsidered, and a method proposed in which the valence excitation energy is no more neglected with respect to the core excitation energy. The divergence of the r^{-4} operators is suppressed, and it is no longer necessary to introduce a cut-off radius. The final result for the second order correction is expressed in terms of the core polarisability, the electric field created by the static and transition distributions (a by product of the gradient algorithm in standard molecular programs), the valence excitation energies and a mean energy typical of core excitation. *Such a method has provided excellent results for Na_2 /23/ using an empirical value for the core polarisability slightly (7%) smaller than the experimental one.* The experimental curves in the ground state and the first excited states are reproduced within a few wavenumbers accuracy.

We should mention also recent work of Konowalow and Fish on Li_2 /24/ in which

Bardsley's pseudo potential /26/ has been included in an *ab initio* treatment, neglecting the V_3 term and hence overestimating the core polarisation effects ; composite curves are presented which are intermediate between *ab initio* calculations /58/ and such results, the two calculations being considered as upper and lower limit for core polarisation corrections.

The results of the four kinds of methods, concerning the ground state of the alkali dimers, are summarised on Table 2, and it is clear that the agreement between theory and experiment is very good.

TABLE 2

Molecular constants for the ground state of the alkali dimers

	$D_e(10^3 \text{ cm}^{-1})$	$R_e(\text{\AA})$	$\omega_e(\text{cm}^{-1})$	Method*	Reference
Li ₂	7.990	2.70	365.8	A	/49/
	8.06	2.73	349	B	/52/
	8.297	2.692	347.1	C	/58/
	8.501	2.672	350	D	/24/
	8.5214	2.673	350	E	/63/
	8.5169			E	/21/
Na ₂	5.72	3.04	163	A	/50/
	5.88	2.96		A	/51/
	6.45	3.05	165	B	/52/
	5.64	3.07	159	B	/55/
	5.72	3.17		C	/59/
	6.020	3.05		D	/23/
	6.024			E	/20/
	6.0226			E	/22/
K ₂	3.06	3.55		A	/51/
	5.16	3.86	99	B	/52/
	4.27	3.85	97	B	/55/
	3.95	3.74	82	D	/62/
	4.19	3.905	92.12	E	/64/

- *
 A effective potential with configuration interaction
 B effective potential with explicit treatment of valence correlation
 C *ab initio* calculations
 D *ab initio* corrected for core-valence correlation effects
 E experiment

CONCLUSION

The intense theoretical activity stimulated by the accuracy of experimental results obtained owing to laser techniques has led to some progress in the description of systems with one and two active electrons.

Concerning alkali-rare gas systems, model potential and pseudo potential techniques, in which the core electrons are simulated by an effective potential, provide a satisfactory description of the physics as far as the ionisation energies are concerned. The rare gas then acts as an additional quantum defect. At short internuclear distances, the accurate evaluation of the core-core interaction is still an open problem. The generalisation of the method to excited rare gas-rare gas interactions demands a precise treatment of the core-core term.

Effective potential methods have long been successful in treating alkali molecular ions. Core polarisation effects are introduced through effective operators which contain a cut-off function to avoid divergence at small r . The results are sensitive to the choice of the cut-off radius, and an unambiguous way of determining this parameter, possibly by fitting to photoionisation cross-sections, should be developed.

The generalisation to two active electron systems such as alkali dimers is performed either by configuration interaction techniques or by the use of correlated functions. A comparison of the two approaches for the treatment of excited and Rydberg states will be possible in the next future. The density functional formalism has been generalised to the treatment of clusters.

Ab initio methods generally provide an overestimation of the bond length, due to a neglect of core polarisation effects. A major improvement has been obtained in the last two years with the introduction of an explicit second order treatment of core-valence correlation in the standard codes. Such a method avoids the difficulties raised by the presence of a cut-off radius in the effective operator method. A spectacular agreement is obtained between theory and experiment for the ground and first excited states of Na_2 . The comparison of this method with effective operator techniques for the treatment of the highly excited states of the dimers and of the collisional ionisation of the alkalis appears as an appealing prospect for future work.

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References

1. Ahmad Bitar R., Lapatovich W.P., Pritchard D.E., Renhorn I. Phys. Rev. Lett. 39 (1977) 1657
2. Tellinghuisen J., Ragone A., Myung S.Kim, Auerbach D.J., Smalley R.E., Wharton L., Levy D.H. J. Chem. Phys. 71 (1979) 1283
3. Masnou-Seeuws F., Philippe M., Valiron P., Phys. Rev. Lett. 41 (1978) 395
4. Hanssen J., McCarroll R., Valiron P., J. Phys. B 12 (1979) 899
5. Valiron P., Gayet R., McCarroll R., Masnou-Seeuws F., Philippe M., J. Phys. B 12 (1979) 53
6. Chebanier de Guerra A., Masnou-Seeuws F. Proc. 13th ICPEAC Berlin (1983) 314 and submitted to J. Phys. B.
7. Pascale J. Phys. Rev. A 28 (1983) 632
8. York G., Scheps R., Gallagher A., J. Chem. Phys. 63 (1975) 1052

9. Mathur B.P., Rothe E.W., Reck G.P., Lightman A.J., Chem. Phys. Lett. 56 (1978) 336
10. Bernheim R.A., Gold L.P., Tipton T. J. Chem. Phys. 78 (1983) 2625
11. Eisel D., Demtröder W., Chem. Phys. Lett. 88 (1982) 481
12. Eisel D., Demtröder W., Müller W., Botschwina P., Chemical Physics 80 (1983) 329
13. Carlson N.W., Taylor A.J., Schawlow A.L., Phys. Rev. Lett. 45 (1980) 18
14. Martin S., Chevalleyre J., Bordas C., Valignat S., Broyer M., Cabaud B., Hoareau A., Chem. Phys. Lett. 87 (1982) 235
15. Leutwyler S., Hermann A., Wöste L., Schumacher E. Chemical Physics 48 (1980) 253
16. Broyer M., Chevalleyre J., Delacretaz G., Martin S., Wöste L. Chem. Phys. Lett. 99 (1983) 206
17. Fuentealba P., Preuss H., Stoll H., von Szentpaly L. Chem. Phys. Lett. 89 (1982) 418
18. Henriët A., Masnou-Seeuws, F. Chem. Phys. Lett. 101 (1983) 535
19. Hessel M.M., Vidal C.R. J. Chem. Phys. 70 (1979) 4439
20. Verma K.K., Bahns J.T., Rajaei-Rizi A.R., Stwalley W.C., Zemke W.T. J. Chem. Phys. 76 (1983) 3599
21. Verges J., Bacis R., Barakat P., Carrot P., Churassy S., Crozet P., Chem. Physics Letters 98 (1983) 203
22. Barrow R.F., Vergès J., Effantin C., Hussein K., D'Incan J. ibid 104 (1984) 179
23. Jeung G.H. J. Phys. B 16 (1983) 4289
24. Konowalow D.D., Fish J.L. Chemical Physics 84 (1984) 463
25. Dalgarno A. Atomic Physics vol. 4 (New York Plenum Press) (1975) 325
26. Bardsley J.N., Case studies in atomic physics vol. 4 (Amsterdam North Holland) (1974) 299
27. Veselov M.G., Schtoff A.V. Opt. Spectrosc. 22 (1967) 457
28. Caves T.C., Dalgarno A. J. Quant. Spectr. Rad. Transf 12 (1972) 1539
29. Bottcher C., Dalgarno A. Proc. R. Soc. A 340 (1974) 187
30. Henriët A., Thèse de 3è cycle (1983) Orsay unpublished
31. Klapisch M. Comput. Phys. Comm. 2 (1971) 239
32. Bottcher C. J. Phys. B 4 (1971) 1140
33. Peach G. J. Phys. B 11 (1978) 2107
34. Valiron P., Roche A.L., Masnou-Seeuws F. and Dolan M.E. J. Phys. B (1984) in press
35. Fermi E. Nuovo Cim. 11 (1934) 157
36. Smirnov B.M. Sov. Phys. JETP 24 (1967) 314
Ivanov O.K. Opt. Spectrosc. 40 (1976) 554
37. Dolan M.E., Masnou-Seeuws F. J. Phys. B 14 (1981) L 583
38. Masnou-Seeuws, F., Boulmer J., Maurin T., Roche A.L., Valiron P., J. Phys. B 15 (1982) 2989
39. Sondergaard N.A., Mason E.A. J. Chem. Phys. 62 (1975) 1299
40. Lamm D.R., Thackston M.G., Eisele F.L., Ellis H.W., Twist J.R., Pope W.P., Gatland I.R., McDaniel E.W. J. Chem. Phys. 74 (1981) 3042
41. Düren R., Tischer H. Chem. Phys. Lett. 79 (1981) 481
42. Düren R., Hasselbrink E., Moritz G. Z. Phys. A 307 (1982) 11
43. Konowalow D.D., Rosenkrantz M.E. Chem. Phys. Lett. 61 (1979) 489
44. Henriët A. to be published
45. Weisheit J.A. Phys. Rev. A5 (1972) 1621
46. Bottcher C. J. Phys. B 6 (1973) 2368
47. Colomb de Daunant I., Vassilev G., Baudon J. and Stern B. Journal de Physique 43 (1982) 591
48. Hennecart D., Masnou-Seeuws F. (1984) submitted to J. Phys. B
49. Watson D.K., Cerjan C.J., Guberman S., Dalgarno A. Chem. Phys. Lett. 50 (1977) 181
50. Bardsley J.N., Junker B.R., Norcross D.W. Chem. Phys. Lett. 37 (1976) 502
51. Valance A. and Nguyen Tuan Q. J. Phys. B 15 (1982) 17
52. Flad J., Igel G., Dolg M., Stoll H., Preuss P. Chemical Physics 75 (1983) 331
53. Chisholm C.D.M., Üpik O., Proc. Roy. Soc. 83 (1964) 541
54. Norcross D.W. Phys. Rev. Lett. 32 (1973) 192
55. Henriët A., Aubert-Frecon M., Le Sech C., Masnou-Seeuws F. (1984) J. Phys. B in press
56. Pluvinaige Ph. Ann. Phys. 5 (1950) 145
Pluvinaige Ph. Journal de Physique 12 (1951) 789

- 57. Aubert-Frecon M., Le Sech C. J. Chem. Phys. 74 (1981) 2931
- 58. Konowalow D.D., Olson M.L. J. Chem. Phys. 71 (1979) 450
- 59. Konowalow D.D., Rosenkrantz M.E., Olson M.L. J. Chem. Phys. 72 (1980) 2612
- 60. Rosmus P., Meyer W. J. Chem. Phys. 65 (1976) 492
- 61. Jeung G.H., Mairieu J.P., Daudey J.P. J. Chem. Phys. 77 (1982) 3571
- 62. Jeung G.H., Daudey J.P., Mairieu J.P. J. Phys. B 16 (1983) 699
- 63. Huber K.P., Herzberg G. Constants of Diatomic Molecules (1979) Van Nostrand Company p 375
- 64. ibid p. 355