Adiabatic Potentials of the Alkali-Rare Gas Atom Pairs *

E. Czuchaj and J. Sienkiewicz

Institute of Physics, University of Gdańsk

Z. Naturforsch. **34a**, 694–701 (1979); received March 26, 1979

The semiempirical potential-model calculations of Baylis have been repeated with some modifications. Firstly, an exact calculation of the Pauli exclusion pseudopotential for the repulsion between alkali core and rare gas atom has been carried out. Secondly, the new atomic radial orbitals proposed by Simons were taken for the calculation instead of those of the Bates-Damgaard type. The adiabatic potentials calculated here have, in general, a similar character as the previous ones obtained by Pascale et al. However, many of them are seriously modified.

1. Introduction

Interatomic potentials are needed for the understanding of various physical processes that occur during the collision of two atoms, such as excitation transfer, quenching of excited states, depolarization, etc. These processes are widely investigated on alkali-noble gas atom pairs. While experiments for such processes are relatively easy to perform, theoretical studies are complicated owing to the difficulty of correctly treating the collision. Except for the ground state, for which the potential energy can be determined experimentally from atomic beam scattering, there is little information concerning the potential energies of excited states of the colliding atoms. So far the latter ones could mostly be deduced from emission experiments as shown by Hedges et al. [1]. A few years ago Carter et al. [2] determined for the first time potential energies for the first excited states of NaNe from differential cross section measurements. It seems that the potential curves of excited states of the alkali-rare gas atom systems can be exactly determined in supersonic expansion experiments (see Smalley et al. [3] and Ahmod-Bitar et al. [4]). To this end one uses single-mode cw dye lasers. Ab initio calculations of adiabatic potentials were available so far only for diatomic systems composed of light atoms. The first four molecular terms for various alkali-rare gas atom pairs have been obtained for the first time by Baylis from pseudopotential calculations [5]. More extensive pseudopotential calculations based on the idea of Baylis have been performed by Pascale and Vandeplanque [6]. The substantial difference between their calculation and that of Baylis is that they included a larger number of states in the atomic basis. The adiabatic potentials of Pascale et al. for the lowest states are quite different from those calculated by Baylis. However, if one compares them with the internuclear potentials deduced from the emission experiments of York et al. [7] for the sodium-rare gas atom pairs one notes considerable discrepancies. To resolve these discrepancies, Saxon et al. [8] have performed configuration interaction (CI) calculations for the NaAr system, which has been studied in recent years extensively both theoretically and experimentally. The CI calculations have given the potential parameters for the ground and first two excited states, which are considerably closer to the values deduced from the experiments of York et al. than the pseudopotential results of Pascale et al. In the present work we have repeated the calculations of Pascale et al. with some modifications. Firstly, we evaluated exactly the Pauli exclusion pseudopotential for the repulsion between an alkali core and a rare gas atom included in the calculation. Secondly, we used for the calculations an atomic basis formed of the radial orbitals proposed by Simons [9]. These functions behave asymptotically like those fo the Bates-Damgaard type but in contrast to them are finite at the origin. In Sect. 2 we outline the pseudopotential method of Baylis and indicate the modifications we have made. Section 3 is devoted to the atomic radial wave functions used in the present calculation. In Sect. 4 we demonstrate some of the obtained potential curves and give a general discussion of our results. All the results of our calculations will be available upon request.

* Work supported by Polish Ministry of Science, Higher Education and Technology project MRI 7.

Reprint requests to Dr. E. Czuchaj, Instytut Fizyki, Uniwersytet Gdański, 80-952 Gdańsk-Oliwa, ul. Wita Stwosza 57, Poland.

0340-4811 / 79 / 0600-0694 $ 01.00/0

2. General Theory

We are not going to describe the Baylis method here in detail. This has been done elsewhere (compare [5] and [6]). Here we present only the basic idea of the method and emphasize the points in which our calculation differs basically from that of Baylis as well as Pascale et al. The Baylis' semiempirical potential model calculation of diabatic potentials of diatomic systems consists in finding the eigenvalues of an effective Hamiltonian of the system, which depends on the internuclear distance of interacting atoms. The Hamiltonian of the system composed of an alkali atom A and a rare gas atom B can be put as

$$H = H_A + H_B + V_{AB}\,, \tag{1}$$

where H_A and H_B are the Hamiltonians of the free atoms A and B, and V_{AB} stands for the interaction between the atoms. In order to obtain the adiabatic potentials of the interacting atoms it is necessary to make important simplifications. It is assumed that in the case of thermal collisions the perturbations of the alkali core and of the rare gas atom are quite small. Thereby both the states of the alkali core and of the rare gas atom may be described by unperturbed atomic wave functions. Only the valence electron of the alkali atom suffers the perturbation. Defining the zero energy of the system when both the atoms are in the ground states and isolated we may write down the Hamiltonian [1], after separating the center of mass motion from the relative nuclear motion, in the form

$$H_e(\boldsymbol{r}, \boldsymbol{R}) = H_A{}^e(\boldsymbol{r}) + V(\boldsymbol{r}, \boldsymbol{R})\,, \tag{2}$$

where $H_A{}^e(\boldsymbol{r})$ is the valence electron Hamiltonian of the free alkali atom, $V(\boldsymbol{r}, \boldsymbol{R})$ is the interaction between the atoms; $\boldsymbol{r}$ and $\boldsymbol{R}$ are respectively the position vectors of the alkali valence electron and of the rare gas atom nucleus relative to the alkali nucleus (see Figure 1). The interaction term $V(\boldsymbol{r}, R)$ constists of two parts: (i) an electrostatic interaction involving an adjustable parameter r_0 which is the radius of a sphere surrounding the noble gas atom, (ii) a repulsive part which simulates the effect of the Pauli exclusion principle. If the alkali valence electron is outside the sphere the electrostatic interaction is taken to be simply that of a polarizable dipole (the rare gas atom) in the field of the alkali electron plus alkali core. When the electron is inside the sphere the electrostatic

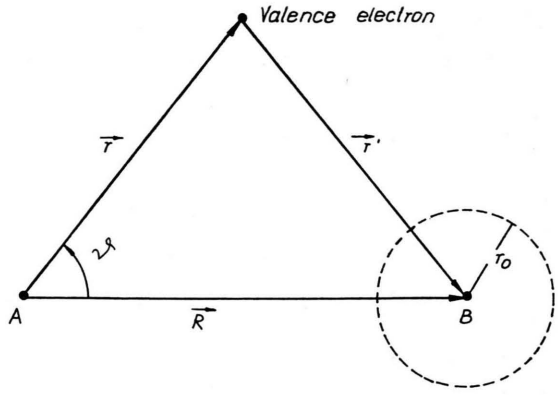

Fig. 1. The model of the alkali-rare gas atom interaction as described in the text.

interaction is taken to be a constant, equal to the average interaction due to an electron at the surface of the sphere. The value of the free parameter r_0, which is treated as a characteristic radius of the rare gas atom must be determined for each pair of the atoms separately. This can be done by fitting the well depth of the calculated ground state potential to that obtained from atomic-beam scattering experiments. Instead of treating the electrons of the system as indistinguishable fermions and consequently taking the antisymmetric wave function it is convenient to treat them as distinguishable particles and to take the wave function to be a simple product of the wave function of the alkali valence electron, of the core and of the rare gas atom. However, to satisfy the Pauli exclusion principle one introduces into the Hamiltonian two additional terms, so-called pseudopotentials, derived on the basis of the Thomas-Fermi statistical atomic model. These have a repulsive character and dominate at small internuclear distances. One of them provides for the core-rare gas atom repulsion and the other tends to exclude the alkali valence electron from the neighborhood of the noble gas atom. Thus one can put the effective potential $V(\boldsymbol{r}, \boldsymbol{R})$ as

$$V(\boldsymbol{r}, \boldsymbol{R}) = F(\boldsymbol{r}, \boldsymbol{R}) + G(\boldsymbol{r}, \boldsymbol{R}) + W(R)\,. \tag{3}$$

Here $F(\boldsymbol{r}, \boldsymbol{R})$ is the electrostatic interaction between the atoms which, under the condition that $R \gg r_0$, takes the form

$$\begin{aligned} F(\boldsymbol{r}, \boldsymbol{R}) &= -\tfrac{1}{2}\alpha_B[E(\boldsymbol{r}, \boldsymbol{R})]^2 \\ &= \tfrac{1}{2}\alpha_B e^2[(\boldsymbol{R}/R^3) - (\boldsymbol{r}'/r'^3)]^2 \end{aligned} \tag{4}$$

for $r' \geqq r_0$ and

$$F(\boldsymbol{r}, \boldsymbol{R}) = -\tfrac{1}{2}\alpha_B e^2[R^{-4} + r_0^{-4}] \quad (5)$$

for $r' < r_0$. Expanding $F(\boldsymbol{r}, \boldsymbol{R})$ in a series of the Legendre polynomials $P_L(\cos\vartheta)$ one gets

$$F(\boldsymbol{r}, \boldsymbol{R}) = \sum_{L=0}^{\infty} F^{(L)}(r, R)\, P_L(\cos\vartheta), \quad (6)$$

where the expansion coefficients $F^{(L)}(r, R)$ can be found in the way described by Baylis. The coefficients $F^{(L)}(r, R)$ are evaluated in the three regions of the r-range defined by the conditions $r \leqq R - r_0$, $R - r_0 < r < R + r_0$ and $r \geqq R + r_0$, respectively. The analitic expressions for $F^{(L)}(r, R)$ are given in the work of Baylis [5]. The pseudopotential $G(\boldsymbol{r}, \boldsymbol{R})$ which represents the effect of the Pauli exclusion principle and concerns the interaction of the alkali valence electron with the rare gas atom can be expressed in terms of the radial electronic charge density of noble gas atom $\varrho_B(r')$ as

$$G(\boldsymbol{r}, \boldsymbol{R}) = (\hbar^2/2m_e)[3\pi^2 \varrho_B(r')]^{2/3}. \quad (7)$$

Its analytic form suitable for the calculation has been suggested by Baylis (see [5]). The other pseudopotential $W(R)$ which simulates the Pauli exclusion principle for the repulsion between an alkali core and a rare gas atom can be written as

$$W(R) = (3\hbar^2/10m_e)(3\pi^2)^{2/3} \cdot \int d^3\boldsymbol{r}\, \{[\varrho_A(r) + \varrho_B(r')]^{5/3} - \varrho^{5/3}(r) - \varrho^{5/3}(r')\}, \quad (8)$$

where m_e is the electron mass. The radial electronic densities are calculated by the simplified self-consistent field method of Gombas [10]. They have the form

$$\varrho(x) = (1/4\pi)\sum_s \zeta(s)\, x^{\alpha(s)} \exp\{-2\beta(s)\, x\}, \quad (9)$$

where the sum is taken over all occupied shells of the atom, the parameters $\alpha(s)$ and $\beta(s)$ are determined by a variational calculation and $\zeta(s)$ are normalization coefficients. An exact calculation of $W(R)$ on a computer is very time-consuming. Therefore, in the previous calculations it was evaluated in an approximate manner as suggested by Baylis. Except for the assumption that the alkali core-rare gas atom repulsion is dominated by the interaction of the outer shells the pseudopotential $W(R)$ in the present work has been calculated exactly. In order to obtain the adiabatic potentials it is necessary to diagonalize the Hamiltonian $H_e(\boldsymbol{r}, \boldsymbol{R})$ in a basis of eigenfunctions of the free alkali Hamiltonian $H_A^e(\boldsymbol{r})$. To this end it is convenient to take the $|(nls)jm_j\rangle$ representation, where an alkali wave function is the product of a radial function multiplied by a spin-orbit coupling function. The atomic radial orbitals used in the previous calculations of Baylis and of Pascale et al. were wave functions of the Bates-Damgaard type [11]. In the present calculation we have used the radial wave functions suggested by Simons [9]. The latter functions in contrast with the previous ones are finite at the origin and can easily be normalized (see following Section).

3. Atomic Radial Orbitals

The radial wave functions of the Bates-Damgaard type which were used by Baylis and Pascale et al. for diagonalization of the Hamiltonian $H_e(\boldsymbol{r}, \boldsymbol{R})$ behave asymptotically like $\exp\{-\sqrt{-2E}\,r\}$ and go to infinity in the limit $r \to 0$. This fact restricts their usefulness. If one wants to calculate some atomic quantities which are primarily dependent on the value of the radial wave function at large r, for example transition integrals, they may be employed with success. On the other hand, expectation values for many other properties cannot be computed. Besides, the determination of appropriate normalization factors of those functions remains another problem. In the pseudopotential model calculation of Baylis some terms of the electrostatic interaction comprise various powers of r in denominator. For this reason instead of taking the Bates-Damgaard functions it seems reasonable to employ the Simons orbitals for the calculation. As is known, in the central field approximation, an atomic wave function may be put in a product form

$$\psi(r, \vartheta, \varphi) = (R(r)/r)\, Y_l^m(\vartheta, \varphi),$$

where the radial orbital $R(r)$ satisfies in atomic units the equation

$$-\frac{1}{2}\frac{d^2R(r)}{dr^2} + \left[\frac{l(l+1)}{2r^2} + V(r)\right]R(r) = ER(r). \quad (10)$$

To include the effects of electron screening Simons has introduced a model potential in the form

$$V(r) = \frac{\lambda(\lambda+1) - l(l+1)}{2r^2} - \frac{Z_{net}}{r}$$

instead of the real potential $V(r)$. In this manner Eq. (10) transforms to the form

$$-\frac{1}{2}\frac{\mathrm{d}^2R(r)}{\mathrm{d}r^2}+\left[\frac{\lambda(\lambda+1)}{2r^2}-\frac{Z_{\mathrm{net}}}{r}\right]R(r)=ER(r) \tag{11}$$

with the solutions being the Whittaker functions

$$R(r)=W_{Z_{\mathrm{net}}/\sqrt{-2E},\,\lambda+1/2}(2\sqrt{-2E}\,r)\,.$$

These functions possess the same long-range behaviour as the Coulomb approximation wave functions (Bates-Damgaard functions), but by an appropriate choice of λ ($\lambda=l-\delta-K$, where δ is the quantum defect and K is any integer) one can make them to be finite at the origin. As suggested by Simons, since at small r the centrifugal term dominates $V(r)$ it is usefull to assume $|\lambda-l|$ to be as small as possible. Thus one obtains that

$$\lambda=l-\delta+\mathrm{Int}(\delta)\,,$$

where $\mathrm{Int}(\delta)$ is the rounded nearest integer value of the quantum defect. Finally, several straightforward algebraic manipulations allow the new orbitals to be normalized and expressed in terms of generalized Laguerre polynomials as

$$\begin{aligned}R(r)=(-)^{n-l-1-\mathrm{Int}(\delta)}\,\mathcal{N}&\left(\frac{2Z_{\mathrm{net}}}{n-\delta}\right)^{l+3/2-\delta+\mathrm{Int}(\delta)}\\&\cdot\exp\{-Z_{\mathrm{net}}\,r/(n-\delta)\}\cdot r^{l+1-\delta+\mathrm{Int}(\delta)}\\&\cdot L^{2l+1-2\delta+2\,\mathrm{Int}(\delta)}_{n-l-1-\mathrm{Int}(\delta)}\left(\frac{2Z_{\mathrm{net}}}{n-\delta}\,r\right)\end{aligned}$$

with

$$\mathcal{N}=\sqrt{\frac{(n-l-1-\mathrm{Int}(\delta))!}{2(n-\delta)\,\Gamma(n+l+1-2\delta+\mathrm{Int}(\delta)}}\,.$$

We recall that the quantum defect δ is introduced according to the well-known formula

$$E=-Z^2_{\mathrm{net}}/2(n-\delta)^2\,.$$

Thus the atomic radial wave functions are characterized by the quantum numbers n and l and by the quantum defect δ.

4. Calculation

In order to obtain the adiabatic potentials it is necessary to calculate all the matrix elements of the Hamiltonian $H_e(\boldsymbol{r}, \boldsymbol{R})$ in an atomic basis and then to diagonalize the matrix. Diagonal elements of the matrix obtained in this manner are the eigenvalues of the Hamiltonian, whereas the columns of the transformation matrix which diagonalizes $H_e(\boldsymbol{r}, \boldsymbol{R})$ are the corresponding molecular eigenvectors. The atomic basis that we use in our calculation does not include so large number of alkali states as that of Pascale et al. However, it is large enough to ensure the stability of the first excited molecular terms of each of the considered systems. For example, for lithium we have taken the following states: 2S1/2, 2P1/2, 2P3/2, 3S1/2, 3P1/2, 3P3/2, 3D3/2 and 3D5/2. For the other alkali atoms the basis has been taken analogically. Based on the convergence of the molecular terms with increasing basis we believe that our adiabatic potentials for lithium are stable from the ground state up to the ones correlated with the 3P3/2 level (compare [16]). The parameters required in the calculation of molecular terms are the alkali energy levels and polarizabilities of the rare gas atoms. All these parameters are the same as in the calculations of Pascale et al. However, the radius r_0 involved in the calculation of the electrostatic interaction energy between the alkali and the rare gas atom was determined for each pair of the atoms separately. This was done by fitting the well depth of the calculated ground state potential to that of Pascale et al. The parameters α and β involved in the expression (9), which gives the radial electronic charge density for the rare gas atoms have been taken from the work of Gombas [10], but those for the alkali cores come from Gombas and Szondy [12]. For the diagonalization we used the well-known Jacobi procedure. In general, the molecular terms obtained in the present work are denoted with the quantum numbers Ω and the alkali states to which they separate for large internuclear distances. Where it is possible they are sometimes denoted according to the notation of Herzberg [14].

5. Results and Discussion

In the present work we have carried out the calculation of the molecular terms for all the alkali-rare gas atom pairs. It is impossible to report here all the adiabatic potentials we have obtained. They will be available upon request. In this Section we present some of the calculated potentials and give a general discussion of the results. In Table 1 are given the potential parameters (well depth and position of minimum) of the first two excited molecular terms for various alkali-rare gas

Table 1. Potential wells of the first two excited states of various alkali-rare gas atom pairs. The values in parentheses refer to the potentials calculated by Pascale et al.

System	$r_0(a_0)$	$A^2\Pi_{1/2}$		$A^2\Pi_{3/2}$	
		ε_m (cm^{-1})	$R_m(a_0)$	ε_m (cm^{-1})	$R_m(a_0)$
LiHe	0.85	59 (17)	4.75 (7.0)	60 (18)	4.5 (6.75)
LiNe	0.6	22 (17)	7.5 (8.0)	23 (18)	7.5 (8.0)
LiAr	1.0	728 (351)	4.5 (5.75)	729 (351)	4.5 (5.75)
LiKr	1.15	1253 (580)	4.5 (5.75)	1254 (580)	4.5 (5.75)
LiXe	1.505	1670 (746)	4.75 (6.0)	1670 (746)	7.5 (6.0)
NaHe	0.8	47 (6)	5.0 (8.0)	52 (11)	5.0 (8.0)
NaNe	0.8	10 (7)	8.25 (9.0)	15 (12)	8.5 (9.0)
NaAr	0.97	506 (276)	5.0 (6.25)	512 (282)	5.0 (6.25)
NaKr	1.1	812 (480)	5.25 (6.25)	817 (485)	5.25 (6.25)
NaXe	1.46	1087 (656)	5.5 (6.5)	1092 (662)	5.5 (6.5)
KHe	0.59	11 (1)	6.25 (15)	28 (7)	6.25 (9)
KNe	0.55	1 (0)	18.0 —	12 (9)	8.25 (10)
KAr	0.925	227 (233)	6.25 (6.75)	246 (252)	6.25 (6.75)
KKr	1.0	372 (417)	6.25 (6.75)	390 (435)	6.25 (6.75)
KXe	1.225	545 (637)	6.5 (7.0)	563 (655)	6.5 (7.0)
RbHe	0.575	0 (0)	— —	19 (6)	7.0 (9.0)
RbNe	0.535	0 (0)	— —	10 (8)	8.5 (10)
RbAr	0.93	82 (164)	7.25 (7.0)	153 (236)	7.25 (7.0)
RbKr	0.975	170 (335)	7.25 (7.0)	243 (408)	7.25 (7.0)
RbXe	1.235	278 (544)	7.5 (7.0)	353 (619)	7.25 (7.0)
CsHe	0.55	0 (2)	— (14.25)	13 (7)	7.25 (9.75)
CsNe	0.525	0 (0)	— —	9 (7)	9.0 (10.25)
CsAr	0.888	10 (83)	8.25 (7.5)	106 (204)	7.75 (7.5)
CsKr	0.955	52 (215)	8.0 (7.5)	167 (350)	7.75 (7.5)
CsXe	1.18	116 (396)	8.0 (7.5)	250 (545)	8.0 (7.5)

atom pairs. For comparison we have given in parentheses the values which refer to the potentials calculated by Pascale et al. We see that for Li and Na our potentials have considerably deeper minima with positions slightly shifted towards smaller internuclear distances as compared to those of Pascale et al. For K they become comparable with the latter ones and for Rb and Cs are shallower and the positions of their minima are slightly shifted towards larger internuclear distances. Besides, as one goes from lighter to heavier rare gas atoms the potential well are, generally, increasingly deep. Figures 2—7 present the ground and some excited potential curves of various alkali-noble gas atom pairs. Figure 2 shows various theoretical and experimental $X^2\Sigma$ and $A^2\Pi$ potential energy curves of the NaAr system. We see that our $A^2\Pi$ curve which differs in the well depth from that of Saxon et al. by about 5 cm^{-1} is closer to the experimental curve deduced from the York et al. experiment [7] than the curve calculated by Pascale et al. Figure 7 presents the ground state potential and the excited ones correlated with the 5D and 7S atomic levels for the CsXe system. For this system we can compare the calculated potential energies to the experimental data of Moe, Tam and Happer [13]. These authors studied pressure induced transitions between the ground state and the corresponding excited states in absorption for the CsXe and RbXe systems. The spectra obtained by them appear to be at considerable variance with the ones which would be expected from the potentials of Pascale et al. The comparison with the absorption spectra indicates that the latter potentials exhibit too much repulsion. In particular the authors deduce that the potential correlated with the 7S atomic level should have a well depth of about 890 cm^{-1}, whereas the same potential calculated by Pascale et al. has the well depth of about 200 cm^{-1}. Our calculation has given 700 cm^{-1} for the well depth. Furthermore the disagreement between the experimental results and the theoretical ones appears to be considerable for all the rare gases and is particularly large for Ne. This was also confirmed by the investigations of Carter et al. [2]. The potential curves determined by them for NaNe from differential cross section measurements show discrepancies of one order of magnitude in com-

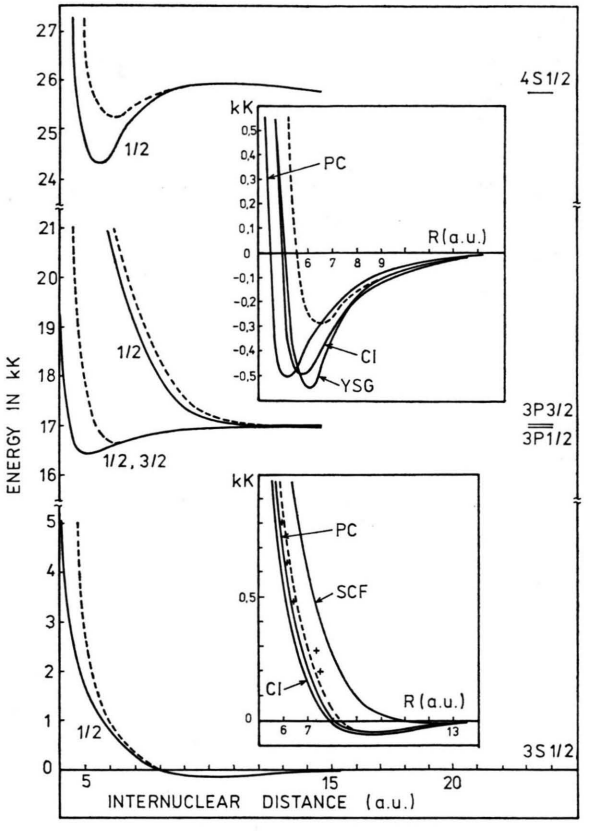

Fig. 2. Potential curves of the first five molecular states of NaAr. The calculated potentials (solid line) are compared to the corresponding potentials of Pascale et al. (dashed line). Each curve is plotted with respect to its own asymptote marked on the right-hand side of the figure. In the inserts our $X^2\Sigma$- and $A^2\Pi$-potentials (PC) are compared with the other available data. CI stands for the configuration interaction calculation of Saxon et al., YSG is the potential deduced from the experiment by York et al., SCF is self consistent field curve of Saxon et al. and the pluses are the scattering data of Malerich and Cross [15] for the ground $X^2\Sigma_{1/2}$ state.

parison with that of Pascale et al. Similar results have been obtained by Riad Ahmod-Bitar et al. [4] in the laser spectroscopic studies of the NaNe molecule produced in a supersonic nozzle expansion. They investigated the $X^2\Sigma \rightarrow A^2\Pi$ transition and found potential parameters for the ground state and the first excited state potentials to be at great variance with those calculated by Pascale et al. and by us. The potentials deduced from their experiment are much deeper than ours. This fact could indicate that the Baylis' pseudopotential method is not able to predict the excited state interaction potentials for NaNe and likely for the other alkali-neon pairs. In our opinion a major portion of the large discrepancy between the experimental and calculated potentials of NaNe can be removed in the framework of the calculation by reducing the radius r_0.

The value of r_0 used in the calculations was determined by the extrapolation method suggested by Baylis*. The well depth of the ground state potential of NaNe calculated in that way is about 1.8 cm^{-1} whereas its value determined experimentally by Carter et al. [2] amounts to 11 cm^{-1}. This means that the value of r_0 that we would obtain by fitting the well depth of the calculated ground state potential to the experimental one would be smaller from the one we used in the calculation. The smaller the value of r_0 is the larger the electrostatic interaction energy becomes. Therefore, the use of a smaller r_0 in the calculation would give a considerable deeper potential of the excited state of NaNe than that we have obtained. The

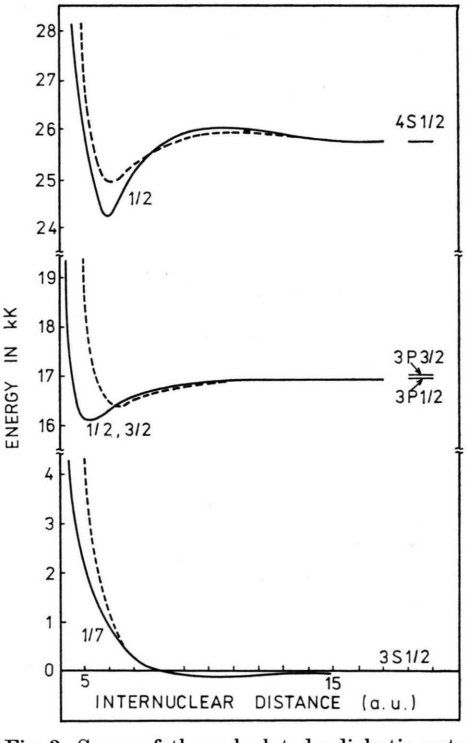

Fig. 3. Some of the calculated adiabatic potentials (solid line) compared to those of Pascale et al. (dashed line) for NaKr.

* When experimental data were not available Baylis used an extrapolation method to fix the corresponding value of r_0.

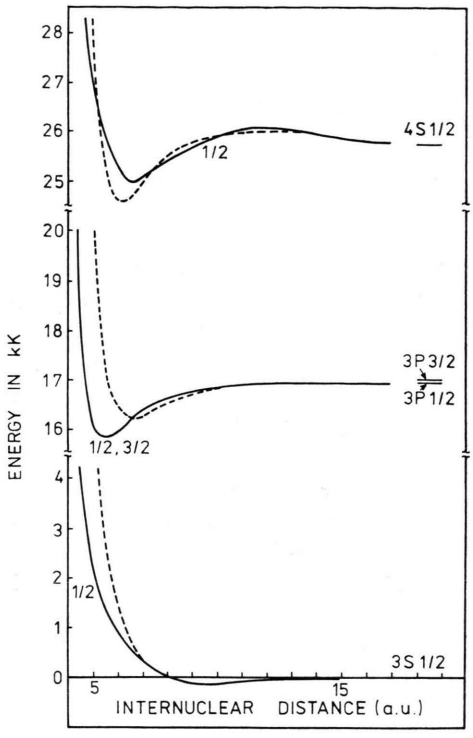

Fig. 4. Same as Fig. 3 for NaXe.

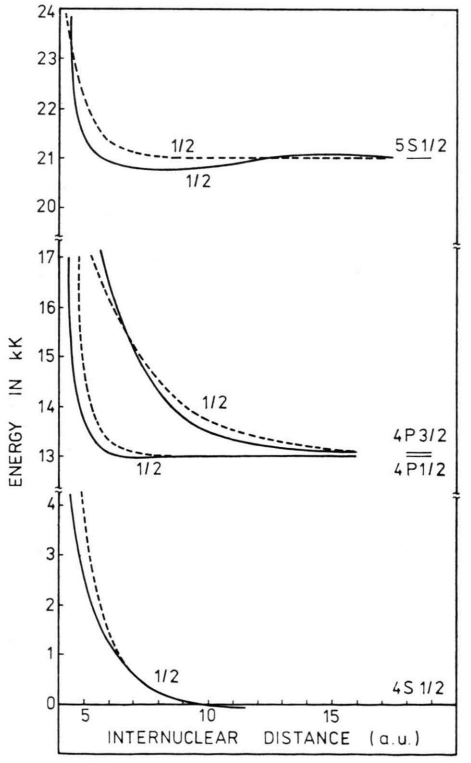

Fig. 5. Same as Fig. 3 for KNe.

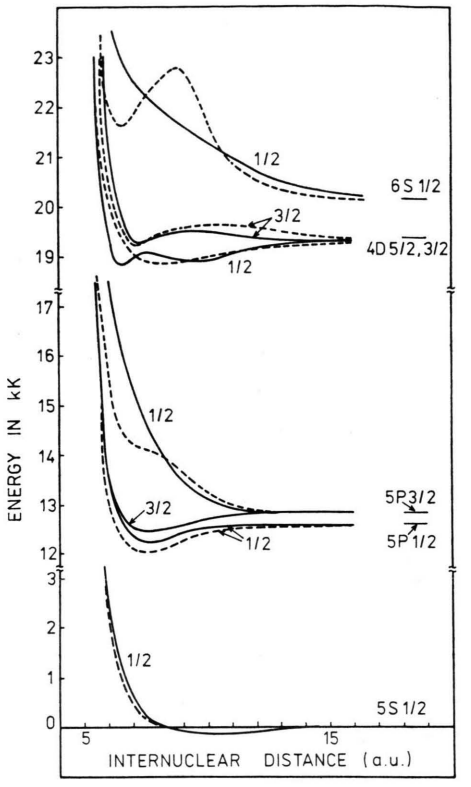

Fig. 6. Same as Fig. 3 for RbXe.

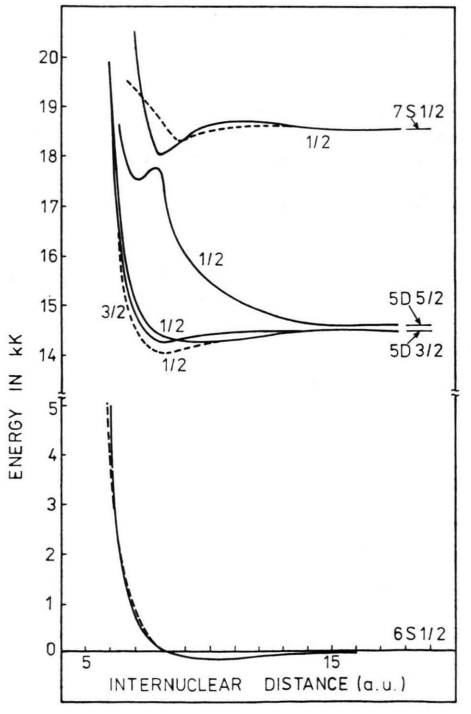

Fig. 7. Same as Fig. 3 for CsXe.

second reason of the disagreement between the calculated and experimental data could be the fact that the pseudopotentials used in the calculation and evaluated on the basis of the Thomas-Fermi statistical atomic model are not adequate to describe the properties of light atoms. Also, we would like to remark that our excited potentials correlated with the S atomic levels are, in general, much deeper than the ones of Pascale et al. Summarizing it is necessary to state that although the present molecular potentials possess a similar character as those calculated earlier with the same method they are considerably modified in comparison with the latter ones. On the other hand the results obtained for NaAr (as in Fig. 2) can be regarded as a proof supporting the use of the modifications, we have made in the pseudopotential model calculations.

6. Conclusion

We have calculated molecular potential curves for various alkali-rare gas atom pairs by using the pseudopotential method previously suggested by Baylis. We have modified the calculation in comparison with that of Pascale et al. by taking into account other atomic radial wave functions as proposed by Simons and by accurate evaluation of the pseudopotential, which provides for alkali core-rare gas atom repulsion due to the Pauli exclusion principle. Although our potentials are, in general, similar to those of Pascale et al. they are considerably modified compared to the latter ones. Comparison of the obtained results for NaAr with the other available data, both theoretical and experimental, indicates that the present calculation gives the molecular potential energies in much better agreement with the other ones than that of Pascale et al. However, it seems that further refinements in the Baylis' method are required. Particularly, an improvement would be necessary to make in calculating the pseudopotential responsible for the exclusion of the alkali valence electron from the neighbourhood of the rare gas atom. In our opinion the approximate method used in the pseudopotential calculations to evaluate the expansion coefficients of that pseudopotential can provide wrong results in the region of small internuclear distances of the atoms, where there are minima of most excited state potentials. That approximation is well justified for large internuclear distances of the atoms but can break down in the region of small ones. The present calculation has also proved that the relatively simple pseudopotential model of Baylis is quite valuable for the determination of excited adiabatic potentials of diatomic systems.

[1] R. E. Hedges, D. L. Drummond, and A. Gallagher, Phys. Rev. A **6**, 1519 (1972).
[2] G. M. Carter, D. E. Pritchard, M. Kaplan, and T. W. Ducas, Phys. Rev. Lett. **35**, 1144 (1975).
[3] R. E. Smalley, D. A. Auerbach, P. S. H. Fitch, D. H. Levy, and L. Wharton, J. Chem. Phys. **66**, 3778 (1977).
[4] R. Ahmod-Bitar and W. P. Lapotowich, Phys. Rev. Lett. **39**, 1657 (1977).
[5] W. E. Baylis, J. Chem. Phys. **51**, 2665 (1969).
[6] J. Pascale and J. Vandeplanque, J. Chem. Phys. **60**, 2278 (1974). CEA Reports (unpublished).
[7] G. York, R. Scheps, and A. Gallagher, J. Chem. Phys. **63**, 1052 (1975).
[8] R. P. Saxon and R. E. Olson, J. Chem. Phys. **67**, 2692 (1977).
[9] G. Simons, J. Chem. Phys. **60**, 645 (1974).
[10] P. Gombas, Pseudopotentiale, Springer, New York 1967.
[11] D. R. Bates and A. Damgaard, Phil. Trans. Roy Soc. London A **242**, 101 (1949).
[12] P. Gombas and T. Szondy, Solution of the simplified S.C.F. for all atoms of the periodic system of elements from $Z = 2$ to $Z = 92$, (Hilger, London 1970).
[13] G. Moe, A. C. Tam, and W. Happer, Phys. Rev. A **14**, 349 (1976).
[14] A. Herzberg, Molecular Spectra and Molecular Structure, Van Nostrand, New York 1956, Vol. 1.
[15] C. J. Malerich and R. J. Cross, Jr., J. Chem. Phys. **52**, 386 (1970).
[16] J. Granier, R. Granier, and F. Schuller, J. Quant. Spectrosc. Radiat. Transfer. **15**, 619 (1975).