Use of dimer potentials to calculate the energy levels of alkali atoms in rare gas matrices

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Use of dimer potentials to calculate the energy levels of alkali atoms in rare-gas matrices[a]

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A simple procedure is described for calculating the energy levels of an alkali atom perturbed by rare-gas neighbors in a solid rare-gas matrix, using alkali-rare-gas dimer potentials available in the literature. Straightforward analysis leads to an expression for the perturbation due to an arbitrary number of rare-gas neighbors in terms of alkali-rare-gas dimer potentials. The results of calculations for Na trapped in Ar are presented and compared with experiment and with earlier pseudopotential calculations.

I. INTRODUCTION

In a previous paper,[1] we reported calculations of the energy-level structure of alkali atoms trapped in rare-gas matrices, using the pseudopotential method originated by Baylis[2] and developed by Pascale and Vandeplanque[3] for the calculation of alkali–rare-gas dimer potentials. Assuming various simple trapping sites in a regular crystal lattice, we calculated the ground-state and excited-state energies of the trapped alkali atom perturbed by pairwise interactions with the neighboring rare-gas atoms. These calculations were made as a function of the alkali position within the trapping site and compared with both experimental emission and absorption spectra.

The principal defect in these calculations was the inaccuracy of the pseudopotential approach to the calculation of the alkali–rare-gas interatomic interaction. In calculations of alkali–rare-gas dimer potentials, the pseudopotential method has been shown[4–6] to yield an insufficiently attractive $A\,^2\Pi$ potential and too repulsive a $B\,^2\Sigma$ potential. Although our pseudopotential calculations were in qualitative agreement with experiment and conclusions could be drawn concerning the size of possible trapping sites, quantitative agreement was poor.

Subsequently, Ossicini and Forstmann[7] also investigated the perturbation of the alkali energy levels in simple trapping sites. Instead of the molecular-physics approach of Ref. 1, they employed a solid-state approach and used a nonlocal pseudopotential to evaluate ground-state and excited-state energy shifts due to the alkali–rare-gas interaction. Their calculations were not made as a function of the alkali position in the site, so they confined themselves to a comparison with experimental absorption spectra. Their conclusions concerning the size of trapping sites for Na in Ar agreed with ours, but their predicted energy shifts were in much better agreement with experimental absorption bands than were the energy shifts we reported in Ref. 1.

The molecular-physics approach to the problem, however, need not be limited by the inaccuracy of the pseudopotential calculation of the alkali–rare-gas interaction. It is possible to express the perturbation of an arbitrary number of rare-gas neighbors in terms of

two-body dimer potentials. By doing this, one can exploit existing experimental or accurate theoretical potentials to obtain much more accurate results than those obtained in Ref. 1. In the process, one also drastically reduces the computation time. It is the purpose of this paper to show how this is done.

Of primary interest for comparison with experiment is the matrix perturbation of the ground state and first excited p state of the alkali atom, because the strongest absorption and emission bands are associated with this s-p transition. As has been pointed out by Baylis,[8] the perturbations of the ground state and of the p state are readily calculated in terms of the two-body $X\,^2\Sigma$, $A\,^2\Pi$, and $B\,^2\Sigma$ potentials.

In the next section, we discuss the theory of this approach. In Sec. III, we present the results of our calculations for Na trapped in Ar and compare them with experiment, with the calculations of Ref. 1, and with the solid-state calculation of Ossicini and Forstmann.

II. THEORY

We wish to calculate the interaction potential between the alkali impurity atom and the rare-gas crystal, using the Born–Oppenheimer approximation to separate the electronic structure of the atoms and the vibrational structure of the crystal. We will assume that the core electrons in the alkali are unaffected by the rare-gas atoms.

The Hamiltonian for the alkali atom–matrix system is:

$$H = H_A(\mathbf{r}) + \sum_k V(\mathbf{r}, \mathbf{R}_k) , \qquad (1)$$

where $H_A(\mathbf{r})$ is the Hamiltonian for the free alkali atom's valence electron. The valence electron's position vector is $\mathbf{r}$ in a coordinate system centered on the alkali core. $V(\mathbf{r}, \mathbf{R}_k)$ is the interaction potential between the alkali atom and a rare-gas atom with position vector $\mathbf{R}_k$. The sum extends over the rare gas atoms surrounding the alkali atom in a given trapping site.

To calculate the energy levels E of the Hamiltonian H, we use first-order degenerate perturbation theory. Let ϵ_i and ψ_i be the eigenvalues and eigenfunctions of H_A. In this basis, the eigenvalues E are obtained by solving

$$\det \left| V_{ij} - (\epsilon_i - E)\delta_{ij} \right| = 0 \ , \tag{2}$$

where

$$V_{ij} = \sum_k \langle \psi_i | V(\mathbf{r}, \mathbf{R}_k) | \psi_j \rangle \ . \tag{3}$$

To calculate the perturbed energy levels of the alkali atom's first excited p state, we will ignore spin-orbit coupling and restrict the basis set used in Eqs. (2) and (3) to the three p-state levels. The matrix elements V_{ij} are thus

$$V_{ij} = \sum_k \langle m_i | V(r, R_k) | m_j \rangle \ , \tag{4}$$

where m_i is the magnetic quantum number of the p state.

The potentials $V(\mathbf{r}, \mathbf{R}_k)$ can be expanded[2] in Legendre polynomials:

$$V(\mathbf{r}, \hat{\mathbf{R}}_k) = \sum_L V_L(\mathbf{r}, \mathbf{R}_k) P_L(\hat{r}, \hat{R}_k) \ . \tag{5}$$

At this point in our previous work (Ref. 1), we proceeded to calculate the $V_L(\mathbf{r}, \mathbf{R}_k)$ by the pseudopotential method. Instead, we now express these in terms of the diatomic $V_{A\Pi}$ and $V_{B\Sigma}$ potentials.

Equation (4) is readily evaluated with the aid of the addition theorem:

$$P_L(\hat{r}, \hat{R}_k) = \sum_M \sqrt{4\pi/(2L+1)} \, Y_{L,M}(\theta, \phi) Y^*_{L,M}(\theta_k, \phi_k) \ . \tag{6}$$

Because of the properties of the spherical harmonics, only the $L=0$ and $L=2$ terms contribute, so Eq. (4) becomes

$$V_{ij} = \sum_k \langle np | V_0(\mathbf{r}, \mathbf{R}_k) | np \rangle \langle m_i | P_0(\hat{r}, \hat{R}_k) | m_j \rangle$$

$$+ \sum_k \langle np | V_2(\mathbf{r}, \mathbf{R}_k) | np \rangle \langle m_i | P_2(\hat{r}, \hat{R}_k) | m_j \rangle \ . \tag{7}$$

Furthermore (Ref. 8), these matrix elements are simply related to the dimer potentials $V_{A\Pi}(R_k)$ and $V_{B\Sigma}(R_k)$. Specifically,

$$V_{A\Pi}(R_k) = \langle np | V_0(\mathbf{r}, \mathbf{R}_k) | np \rangle - 1/5 \langle np | V_2(\mathbf{r}, \mathbf{R}_k) | np \rangle \ , \tag{8a}$$

and

$$V_{B\Sigma}(R_k) = \langle np | V_0(\mathbf{r}, \mathbf{R}_k) | np \rangle + 2/5 \langle np | V_2(\mathbf{r}, \mathbf{R}_k) | np \rangle \ . \tag{8b}$$

Upon calculating the angular factors $\langle m_i | P_L(\hat{r}, \hat{R}_k) | m_j \rangle$ with the aid of Eq. (6), one finds that

$$V_{11} = V_{33} = \sum_k [1/2(1 + \cos^2 \theta_k) V_{A\Pi}(R_k)$$

$$+ 1/2 \sin^2 \theta_k V_{B\Sigma}(R_k)] \ , \tag{9a}$$

$$V_{22} = \sum_k [\sin^2 \theta_k V_{A\Pi}(R_k) + \cos^2 \theta_k V_{B\Sigma}(R_k)] \ , \tag{9b}$$

$$V_{12} = \sum_k \{1/\sqrt{2} \sin \theta_k \cos \theta_k$$

$$\times \exp(-i\phi_k)[V_{A\Pi}(R_k) - V_{B\Sigma}(R_k)]\} \ , \tag{9c}$$

$$V_{13} = \sum_k \{1/2 \sin^2 \theta_k \exp(-2i\phi_k)[V_{B\Sigma}(R_k) - V_{A\Pi}(R_k)]\} \ , \tag{9d}$$

$$V_{12} = V^*_{21} = -V_{23} = -V^*_{32} \ , \tag{9e}$$

$$V_{13} = V^*_{31} \ , \tag{9f}$$

where θ_k and ϕ_k relate to the position of the kth Ar atom in a coordinate system centered on the alkali core.

One is now in a position to use $V_{A\Pi}$ and $V_{B\Sigma}$ potentials available in the literature to calculate the perturbed p-state energies for rare-gas atom configurations in various model trapping sites. One simply evaluates the potentials and angles θ_k and ϕ_k for each Ar atom, performs the sums in Eqs. (9), and solves Eq. (2).

The calculation of the matrix perturbation of the alkali ground s state is even easier, since the $X^2\Sigma$ dimer potentials are simply additive.[8]

III. RESULTS

We present here the results of our calculations of the perturbed ground state and p-state energies of Na trapped in a regular Ar crystal, using Na–Ar potentials from the literature which are more accurate than pseudopotential calculations. For the ground-state calculation, we used the $X^2\Sigma$ potential determined experimentally by Tellinghuisen et al.[6] For the $A^2\Pi$ contribution to the p-state energy, we used a potential function which averaged the experimental potentials obtained by Tellinghuisen et al. and by York et al.[4] For the $B^2\Sigma$ contribution, we used the theoretical potential of Saxon et al.,[5] which was based on CI calculations.

We computed perturbed ground state and p-state energies, as a function of the Na atom's position, in three model trapping sites: a substitutional site, a 2-Ar vacancy, and a 4-Ar vacancy. These sites were chosen, not because they are necessarily realistic, but because they allow comparison with our previous pseudopotential calculations and with the pseudopotential calculations of Ossicini and Forstmann. Contributions from Ar atoms within a spherical volume of radius 10 Å were included. The results are shown in Figs. 1–3, where the p-state energies are compared with the pseudopotential calculations of Ref. 1. The qualitative behavior of the perturbed energy levels is similar to that obtained in Ref. 1, but the use of the more accurate dimer potentials leads to a far weaker perturbation of the p state, in accord with experiment.

Na trapped in Ar matrices exhibits[9,10] a strong absorption band near the wavelength of the free-atom D-lines and weaker bands shifted to shorter wavelengths. The two strongest bands have a triplet structure. The fluorescence produced by excitation of the absorption bands is substantially red shifted and very broad. The main features of the observed spectra are summarized in Table I.

Assuming that the Na atom is initially at the center of a particular trapping site, the peaks of the corresponding absorption band would be determined by the difference in energy between the perturbed s- and p states, and this wavelength is indicated in Figs. 1–3. Once excited, the Na atom and its Ar neighbors relax to a minimum in the interaction potential, resulting in a red-shifted fluorescence. Considering only motion of
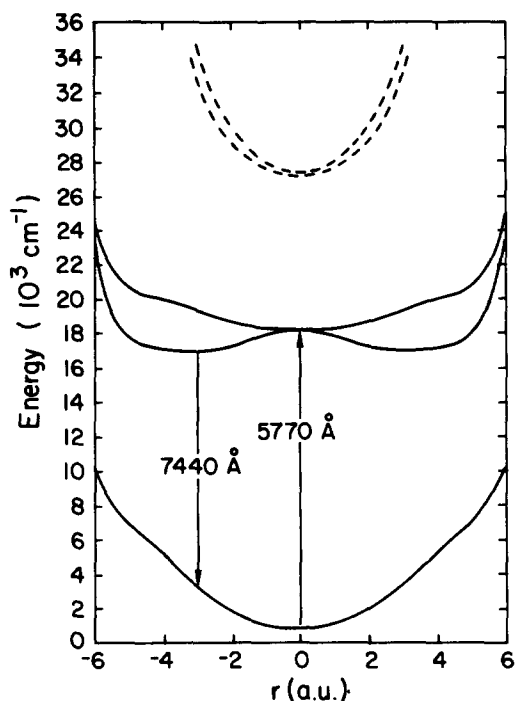
FIG. 1. The perturbed 3s and 3p energy levels of a Na atom in a substitutional site within a regular Ar fcc lattice. The solid lines show the results of the present calculation of the Na energy as a function of position on a line passing through the center of the site and a next-nearest Ar neighbor. The dashed curve shows the results for the 3p energy obtained in Ref. 1. Also given are the corresponding peak absorption and emission wavelengths.
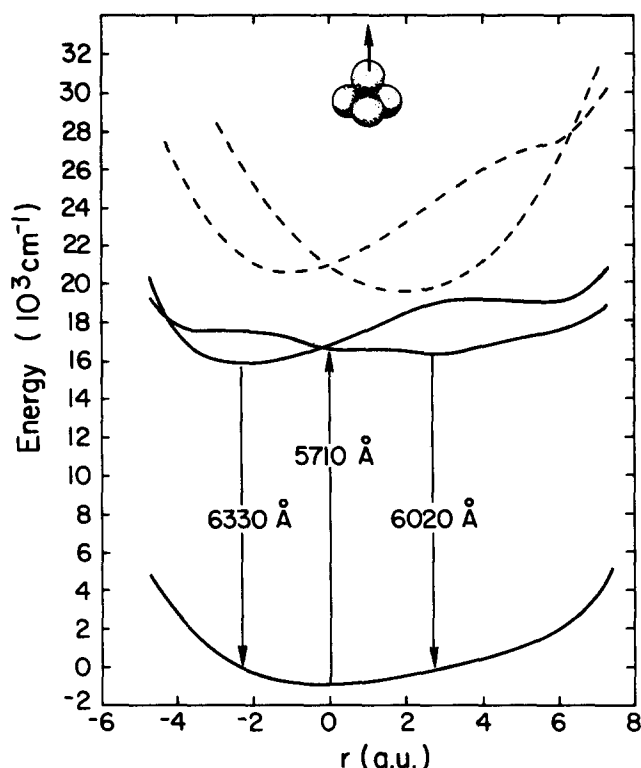

FIG. 3. The perturbed 3s and 3p energy levels of a Na atom in the 4-Ar vacancy pictured in the figure. The energies are shown as a function of position along a line passing through the center of the site and the center of one of the removed Ar atoms. The dashed curve shows the results obtained in Ref. 1. Also shown are the corresponding peak absorption and emission wavelengths.
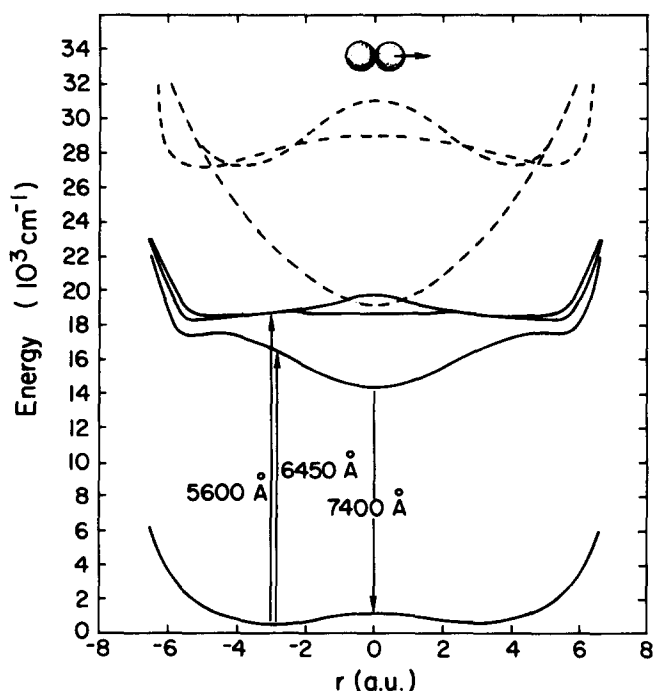

FIG. 2. The perturbed 3s and 3p energy levels of a Na atom in a vacancy obtained by removing two adjacent Ar atoms from a regular lattice. The energies are shown as a function of position along the line of axial symmetry. The dashed curve shows the results obtained in Ref. 1. Also shown are the corresponding peak absorption and emission wavelengths.

the Na atom within a site of fixed Ar atoms (admittedly an oversimplification), we have indicated in Figs. 1–3 an emission peak wavelength for each site.

Comparison with Table I shows that none of the simple vacancy sites considered here yields potentials that exactly reproduce the experimental results. This is not surprising, since it is unlikely that the Na atom is trapped in a simple vacancy within an undistorted, regu-

TABLE I. A summary of the principal features of absorption and emission spectra observed (Ref. 9) for Na in an Ar matrix at 10 K. The emissions from bands A and B have two peaks, and the secondary peak is given in parenthesis.

Band	Absorption peak (Å)	Emission peak (Å)	Wavelength range (Å)
A	5945 5875 5775	7000 (7700)	6500–8700
B	5540 5450 5360	6800 (7600)	6400–7800
C	5145	7600	8000–9000
D	4800		

lar lattice; the Na–Ar interaction is too repulsive. The Na–Ar equilibrium separation is 4.99 Å; the Ar–Ar separation is 3.76 Å. One would expect numerous irregular sites of varying size to be formed.

This picture is borne out experimentally. It is evident[9,10] that the absorption and emission bands arise from a multiplicity of sites of varying thermal stability. Furthermore, the emission band obtained upon exciting an individual absorption band generally has more than one peak. The relative amplitudes of these peaks varies with deposition conditions, indicating that even individual absorption bands are actually superpositions of overlapping bands from distinct trapping sites.

Nevertheless, the present results demonstrate that the absorption and emission spectra of Na in Ar are consistent with existing knowledge of the Na–Ar two-body interaction. The 4-Ar vacancy considered here is large enough to accommodate the Na atom with no compression, and the substitutional site represents a site with high compression. It is reasonable to expect that the actual site volumes lie between these two extremes. The wavelengths obtained for both these extremes are in reasonable accord with what is observed, and this contrasts sharply with our previous pseudopotential calculations, which led to extremely blue-shifted wavelengths.

Indeed the 4-Ar vacancy is an excellent candidate for the thermally stable blue-shifted absorption B, which was suggested in Ref. 1 but made more plausible by the calculations of Ossicini and Forstmann. Their calculation of energy-level shifts for this site agrees well with the present calculation of the absorption band wavelength. Our calculation of the red-shifted emission wavelength produces too small a red shift, but the discrepancy with experiment is not great and may be due to the fact that we have not included relaxation of the matrix in this calculation.

The triplet structure of the two major Na absorption bands may be due to the Jahn–Teller effect, as is commonly believed, but minor distortions of the lattice site will also lead to a splitting of the energy levels we calculate.

The 2-Ar vacancy, with its axial symmetry, produces a doublet absorption which is observed in many alkali-matrix systems, but the departure from spherical symmetry is so great that the doublet splitting is far larger than what is observed.

In Ref. 1, we concluded, on the basis of the ground-state Na–Ar interaction, that a substitutional site is too small to accommodate a Na atom, and this conclusion was also reached by Ossicini and Forstmann. We can, however, compare our present calculation of the energy-

level shifts for this site with their shift calculations. Although our calculations agreed with theirs for the 4-Ar vacancy, our present results predict an absorption band blue shift of only 350 cm⁻¹ whereas they predicted a shift of 2000 cm⁻¹.

To make further progress in the analysis of matrix-isolated alkali spectra, it would seem necessary to use computer simulations of matrix growth to generate realistic trapping sites. The calculational method described here would be easily applied to such sites, and the small computation time involved with this technique should permit the investigation of relaxation effects by allowing motion of both the alkali and the neighboring rare-gas atoms.

IV. CONCLUSION

The calculation of the matrix-perturbed alkali energy levels is greatly simplified by expressing the perturbing interaction in terms of dimer potentials. The use of accurate dimer potentials leads to a correspondingly more accurate determination of the matrix perturbation and will permit a realistic study of relaxation effects following excitation of the alkali atom.

In addition, as accurate dimer potentials for higher excited states become available, the same approach can be taken to calculate the matrix perturbation of alkali energy levels lying above the first excited state for comparison with experiment. Absorption and emission spectra for the $(n - 1)d$ and $(n + 1)s$ states of Rb and Cs have already been observed.[11]

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