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Pseudopotential molecular-structure calculations for NaHe and CsHe

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Molecular-structure calculations have been performed to obtain the adiabatic potentials for ground-state and excited NaHe and CsHe systems. They use l-dependent pseudopotentials for e-He and e-Na$^+$ (or Cs$^+$) interactions. The adiabatic potentials obtained for the low-lying states of NaHe and for some excited states of CsHe are in good agreement with recent experimental data, indicating a large improvement on all previous calculations for these systems.

So far extensive Gombas-type pseudopotential molecular-structure calculations for alkali—rare-gas systems[1,2] have been very useful for many semiquantitative interpretations of various collisional processes. These calculations used an l-independent (or local) statistical pseudopotential to represent the interaction between the alkali valence electron and the rare-gas atom. With growing amounts of accurate experimental data it has been manifest that an improvement of these calculations is necessary, and especially for the lightest rare-gas atoms. Some attempts to improve them have been made recently[3,4] but they were completely unsuccessful in the cases of He and Ne. However recent works[5–9] have shown that reliable adiabatic potentials for alkali-He (or Ne) systems could be obtained by using model potential or pseudopotential techniques. From these works it is clear that a local potential can be used in model potential calculations, but only with the important condition that the electron wave function be orthogonal to the orbitals of the cores; while in pseudopotential calculations a nonlocal potential has to be used. In both techniques an effective potential is defined so as to represent the potential experienced by the valence electron. It simulates the screening effect of the core electrons. In the pseudopotential technique it simulates also by a repulsive potential the antisymmetry effects due to the Pauli principle. Therefore, in this latter technique the effective potential is l dependent and the lowest radial wave function for an l series is nodeless. For molecular-structure calculations the pseudopotential technique seems to be the most appropriate[10] as the core orbitals have not to be included in the atomic basis set expansion of the molecular wave function. Up to now the l-dependent pseudopotential technique has rarely been used for alkali—rare-gas systems[9] and the model potential technique seems to be cumbersome in the cases of cores with a large number of electrons. It is desirable, however, that extensive but accurate molecular-structure calculations be made for these systems as many accurate experimental data are available. We have undertaken such calculations with l-dependent pseudopotentials. We have chosen to study first the alkali-He systems since it is for these systems that the use of a local statistical pseudopotential in our previous calculations[2] is the most questionable. In this Communication we present some low-lying states of NaHe and some excited states of CsHe for which recent experimental data[11,12] have been found in variance with theoretical predictions.

For the alkali—rare-gas systems the many-body problem of the interaction may be reduced to a three-body interaction. Then, in the approximation of Born and Oppenheimer, the adiabatic potentials $E_i(R)$ which depend on the internuclear distance R are obtained by diagonalizing the effective Hamiltonian for the valence electron e^-:

$$[-\tfrac{1}{2}\nabla^2_{\vec{r}} + V_A(\vec{r}_A) + V_B(\vec{r}_B) + V_{\mathrm{CT}}(\vec{r},\vec{R}) + V_{\mathrm{CC}}(R) - E_i(R)]\psi_i(\vec{r},R) = 0 \;, \qquad (1)$$

where $\vec{r}_X, X \equiv A,B$, are the position vectors of e^- with respect to the alkali core (A) and the He atom (B). $V_X(\vec{r})$ is the interaction between e^- and the core X and has the form

$$V_X(\vec{r}) = V_X^{\mathrm{sr}}(\vec{r}) - \frac{Z_X}{r} - \frac{1}{2}\frac{\alpha_{dX}}{(r^2+d_X^2)^2} - \frac{1}{2}\frac{\alpha'_{qX}}{(r^2+d_X^2)^3} \;, \qquad (2)$$

where V_X^{sr} is a short-range potential; Z_X is the charge of X; α_{dX} is the static dipole polarizability of X; α'_{qX} is an effective quadrupole polarizability for X that we define as

$$\alpha'_{qX} = \alpha_{qX} - 6\beta_X + 2\alpha_{dX} d_X^2 \qquad (3)$$

in order to take into account the dynamical correction $-6\beta_X$ to the static quadrupole polarizability α_{qX}, and the contribution of the dipole interaction term to the r^{-6} expansion term of $V_X(r)$ at large values of r; d_X is a cutoff radius.

The short-range potential $V_X^{\mathrm{sr}}(\vec{r})$ is a l-dependent pseudopotential which simulates the Pauli principle and the screening effect of the core electrons:

$$V_X^{\mathrm{sr}}(\vec{\mathrm{r}}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} V_{Xl}^{\mathrm{sr}}(r) |y_{lm}(\hat{r})\rangle \langle y_{lm}(\hat{r})| \ , \tag{4}$$

where $|y_{lm}(\hat{r})\rangle$ is a spherical harmonic, and V_{Xl}^{sr} is a Gaussian-type potential[10]

$$V_{Xl}^{\mathrm{sr}}(r) = C_{Xl} \exp(-D_{Xl} r^2) \ . \tag{5}$$

For Na and Cs atoms the parameters α_{dA}, α'_{qA}, d_A, C_A, and D_{Al} were taken from Table 13 of Ref. 10. For He atom we took $\alpha_{dB} = 1.3834$,[13] $\alpha_{qB} = 2.3265$,[14] and $\beta_B = 0.706$.[15] Atomic units (a.u.) are used unless specified. The other parameters were determined by fitting recent experimental phase shifts[16] for e^--He scattering and the value[17] 1.177 for the scattering length. The best fit obtained for these parameters is $d_B = 1.0$, $C_{B0} = 2.03$, $D_{B0} = 0.463$, $C_{Bl\geq 1} = -1.0$, and $D_{Bl\geq 1} = 1.0$. With these values, the experimental phase shifts are reproduced over the energy range (0.58–20.0 eV) to better than 3% for the *s* wave, 23% for the *p* wave, and 15% for the *d* wave; and the calculated scattering length is 1.179.

$V_{\mathrm{CT}}(\vec{\mathrm{r}}, \vec{\mathrm{R}})$ is the well-known three-body interaction or cross term (see Ref. 18 and references therein) resulting from the polarization of the He atom by both e^- and the alkali core. It has to be included for having the correct behavior of the interaction at large values of R. We have taken

$$V_{\mathrm{CT}}(\vec{\mathrm{r}}_B, \vec{\mathrm{R}}) = -\frac{\alpha_{dB}\xi}{(R^2+d_B^2)(r_B^2+d_B^2)} - \frac{1}{2}\frac{\alpha''_{qB}(3\xi^2-1)}{(R^2+d_B^2)^{3/2}(r_B^2+d_B^2)^{3/2}} \ , \tag{6}$$

where $\alpha''_{qB} = \alpha_{qB} + 2\alpha_{dB} d_B^2$, and $\xi = \hat{r}_B \cdot \hat{R}$ (note that $\vec{\mathrm{R}}$ is the position vector of B with respect to A).

$V_{\mathrm{CC}}(R)$ is a core-core interaction that we have defined as

$$V_{\mathrm{CC}}(R) = V_{\mathrm{CC}}^{\mathrm{sr}}(R) - \frac{1}{2}\frac{\alpha_{dB}}{(R^2+d_B^2)^2} - \frac{1}{2}\frac{\alpha''_{qB}}{(R^2+d_B^2)^3} \ , \tag{7}$$

where $V_{\mathrm{CC}}^{\mathrm{sr}}(R)$ is a short-range interaction of the form

$$V_{\mathrm{CC}}^{\mathrm{sr}}(R) = a \exp(-br) \ . \tag{8}$$

For the Na^+-He interaction we have chosen to define the parameters a and b by fitting *ab initio* calculations[19] of the $X\,{}^1\Sigma^+$ potential of $\mathrm{Na}^+\mathrm{He}$. The values obtained, $a = 52.681$ and $b = 2.488$, give a well-depth $D_e = 241$ cm^{-1} at $R_e = 4.50$ a.u. for the $X\,{}^1\Sigma^+$ potential, in very good agreement with $D_e = 245$ cm^{-1} at $R_e = 4.50$ a.u. obtained when the experimental data of Ref. 20 are fitted. An asymptotic method[21] has found $D_e = 199$ cm^{-1} at $R_e = 4.80$ a.u. For the Cs^+-He interaction we have chosen to define the parameters by fitting the experimental data of Ref. 22. The values obtained, $a = 49.156$ and $b = 1.875$, give a well-depth $D_e = 44$ cm^{-1} at $R_e = 7.0$ a.u., in good agreement with $D_e = 40$ cm^{-1} at $R_e = 7.5$ a.u. determined in Ref. 21.

We have used a molecular code developed by B. R. Junker to calculate the interaction energies. The spin-orbit interaction was not included for these calculations. The molecular wave function $\psi_i(\vec{\mathrm{r}}, R)$ was expanded over a large basis set of Slater-type orbitals (STO) on center A which includes *s, p, d, f,* and *g* orbitals (27 STO for Σ states, 36 for Π states, and 24 for Δ states). The nonlinear parameters of the STO were optimized at $R = \infty$ and then kept constant at every R. The average error in the ionization energies of the 13 lowest levels is better than 5×10^{-5} a.u. for Na and 10^{-4} a.u. for Cs.

Our results for the NaHe $X\,{}^2\Sigma$ and $A\,{}^2\Pi$ state potential curves are shown in Fig. 1 along with the experimental data of Havey *et al.*[11] Because in the determination of the experimental potentials there is a free parameter to be fixed, these data were renor-

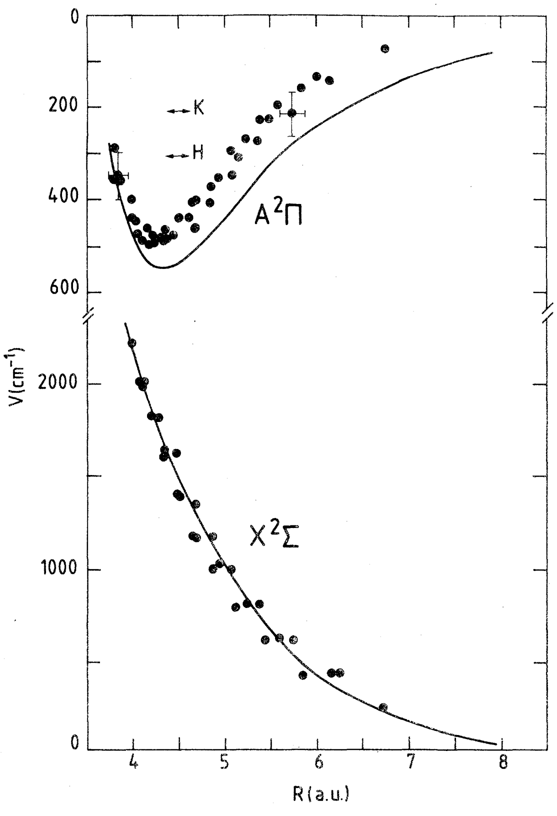

FIG. 1. Potential curves for the $X\,{}^2\Sigma$ and $A\,{}^2\Pi$ states of NaHe. Theory: solid line, present work; the arrows indicate the position of the well predicted by the *ab initio* calculations of Krauss *et al.* (Ref. 19) (K) and by model potential calculations of Hanssen *et al.* (Ref. 7) (H). Experiment: full circles, results of Havey *et al.* (Ref. 11); the radial scale is fixed at $R = 4.0$ a.u.

malized to our calculated $X\,^2\Sigma$ potential at $R=4.0$ a.u. by taking $R \rightarrow (R^3+\Delta R_0^3)^{1/3}$ with $\Delta R_0=0.18$ a.u. Our $X\,^2\Sigma$ potential curve is in excellent agreement with the experimental data while the $A\,^2\Pi$ potential curve is just outside the lower limit of the data. Our values of $D_e=535$ cm^{-1} and $R_e=4.40$ a.u. for the $A\,^2\Pi$ potential curve compare much more favorably with the experimental values ($D_e=480 \pm 50$ cm^{-1}, $R_e=4.4 \pm 0.2$ a.u.) than do the values obtained by Krauss *et al.*[19] from *ab initio* calculations ($D_e=210$ cm^{-1}, $R_e=4.53$ a.u.) and those obtained by Hanssen *et al.*[7] from model-potential calculations ($D_e=299$ cm^{-1}, $R_e=4.58$ a.u.), indicating a significant improvement on these calculations. The differences observed between the present results and those of Hanssen *et al.* cannot be attributed to the estimation of the core-core interaction since it is the same in both calculations. They may be due in part to the use of very different cutoff functions for the polarization interactions. They may also result in part from differences in reproducing the experimental phase shifts wih the e^--He interactions, though the local potential of Valiron *et al.*[6] (with the orthogonality constraints) used by Hanssen *et al.* in the calculation of the NaHe interaction energies gives phase shifts of quality comparable to ours. It seems more likely that the differences observed in the two calculations are inherent to the method used.

Our calculated potentials for the $E\,^2\Sigma\,5D$ and the $F\,^2\Sigma\,7S$ states of CsHe are reported in Fig. 2 along with the experimental data of Ferray *et al.*[12] We have adopted as these authors have done, to plot the excited potentials versus the ground-state potential since it allows us an unambiguous comparison of the data. The fact that the spin-orbit interaction was not included in our calculations should not affect the present comparisons since the $E\,^2\Sigma$ potential curve is found strongly repulsive in the internuclear distance range considered ($R \simeq 5-10$ a.u.). The agreement between our results and the experimental ones is quite remarkable considering the difficulty in the determination of the experimental potentials.[12] The present calculations confirm the strongly repulsive character of the $E\,^2\Sigma$ potential curve which was not predicted by calculations[2,3] using a local statistical pseudopotential, indicating a considerable improvement on these calculations. The present calculations confirm also the presence of an avoided crossing between the potential curves of the $E\,^2\Sigma$ and $F\,^2\Sigma$ states which could explain the large cross section for the quenching of the $7S_{1/2}$ to the $5D_{1/2}$ in Cs-He collisions as suspected by Sayer *et al.*[23] Its position is about $R=6.65$ a.u. where the splitting between the potential curves is about 100 cm^{-1}. Our calculated $F\,^2\Sigma$ potential curve presents a potential barrier of about 200 cm^{-1} at $R \simeq 10$ a.u.

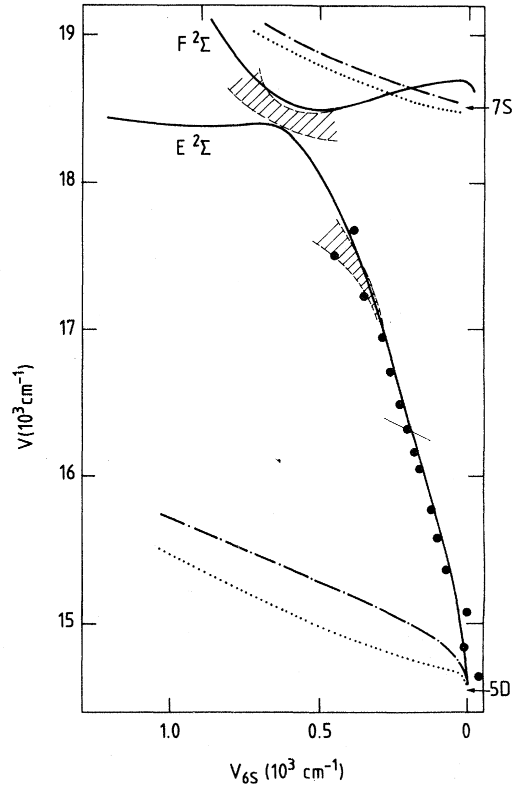

FIG. 2. Potentials for the $E\,^2\Sigma\,5D$ and $F\,^2\Sigma\,7S$ states of CsHe plotted vs the $X\,^2\Sigma\,6S$ potential (see text). Theory: solid line, present work; dash-dotted line, results of Pascale and Vandeplanque (Ref. 2); dotted line, result of Czuchaj and Sienkiewicz (Ref. 3). Experiment: full circles and hatching, data of Ferray *et al.* (Ref. 12).

In conclusion, we have reported in this Communication some calculated adiabatic potentials for low-lying states and more highly excited states of NaHe and CsHe for which comparison with both previous calculations and experimental data was possible. The present results compare much more favorably with experimental data than do all previous calculations, indicating a large improvement in the calculation of the potential curves alkali-He molecule by using an l-dependent pseudopotential technique. They show also that CsHe can be treated without any more difficulty than the lightest alkali-He systems. The results that we have reported here are quite representative of the reliability of our l-dependent pseudopotential calculations. Results on the other alkali-He systems indicate similar agreement with experimental data. For example our calculations for the $^2\Delta\,3D$ state of LiHe find a well-depth $D_e \simeq 510$ cm^{-1} at $R_e \simeq 3.75$ a.u., in good agreement with the very recent experimental values of Havey[24] ($D_e=430 \pm 70$ cm^{-1} at $R_e=3.6 \pm 0.1$ a.u.). Details of our calculations for all alkali-He systems and comparisons with available experimental and theoretical results will be reported in a forthcoming paper.

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