Model-Potential Calculations on the Molecular System NaNe

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Calculations for the $X^2\Sigma$, $A^2\Pi$, and $B^2\Sigma$ states of the NaNe molecular system are reported. The electron-neon interaction is represented by a local potential together with an explicit orthogonality condition to the neon orbitals. The well depth and location are $D = 7.8$ cm^{-1} at $r_m = 10$ a.u. for the $X^2\Sigma$ state and $D = 132$ cm^{-1} at $r_m = 5$ a.u. for the $A^2\Pi$ state, in excellent agreement with the laser-spectroscopy results of Ahmad-Bitar *et al.*

The existence of accurate experiments on the Na-Ne system at thermal energies, either involving refinements in the traditional techniques used for line-broadening, depolarization, and fine-structure transition measurements[1-3] or developing new promising techniques in the field of collision spectroscopy (Carter *et al.*[4]), reveals a need for precise theoretical calculations. More recently, the new experiment of laser spectroscopy of loosely bound Na-Ne molecules achieved by Ahmad-Bitar *et al.*[5] is a challenge for theorists.

The currently used *ab initio* molecular calculations do not seem at the present time well adapted to the problem. In order to obtain an accurate representation of the long-range polarization forces, one must introduce a large number of configurations, making the calculations expensive and the physical interpretation difficult. In contrast, taking account of the fact that *at thermal energies only one electron is active during a Na-Ne collision,* the semiempirical methods reduce the 21-electron problem to the study of *one electron* in the field of Na$^+$ and Ne. Both the calculations and the physical interpretation are then straightforward. Unfortunately, concerning the Na-He and Na-Ne systems,[6] there is a wide discrepancy between the pseudopotential calculations of Baylis[7] and Pascale and Vandeplanque[8] and the model-potential results of Bottcher.[9] Moreover, the poor agreement with the experiments[5] cannot be attributed to experimental uncertainties and the question arises of how reliable results can be obtained with such methods.

The work presented here is an application of the method proposed by Valiron *et al.*[6] which will be presented with more details elsewhere.[10] We have shown that the major difficulty lies in the representation of the electron-neon interaction V_g. Indeed, the determination of the electron-Na$^+$ interaction V_a—by adjusting a parametrized potential so that the eigenvalues of the Schrödinger equation reproduce the sodium atomic energy levels—is now a well-solved problem.[11,12] The choice of V_g is more delicate:

(i) It is important to ensure that the potential V_g can reproduce low-energy scattering data. This was not the case in the earlier pseudopotential calculations.[7,8] However, Malvern and Peach[13] have proposed recently a pseudopotential that is fitted to s-wave scattering data. They obtain NaNe molecular curves that are in much better agreement with experiments.[5]

(ii) If one assumes the neon atom to be frozen in the $^1S_0$ ground state, the application of the Pauli principle to the active electron leads to orthogonality conditions between the wave function of this electron and the 1s, 2s, and 2p orbitals of the neon atom.[10,14,15] The existence of a repulsive short-range potential in the pseudopotential method can be interpreted as a way of taking account of the Pauli principle.[7] But the orthogonality conditions being different for s and p scattered waves and negligible for higher-order partial waves, *an l-independent potential can lead to unsatisfactory results.*[10,15,16]

In the model potential proposed by Bottcher, Dalgarno, and Wright,[17] the electron-neon interaction is represented by a local five-parameter attractive potential V_g, containing three bound states. These bound states are necessary to reproduce correctly the zero-energy limit of the phase shifts (2π for s wave, π for p wave). The wave function of the active electron is then automatically orthogonal to bound-state wave functions. These states appear as unphysical solutions of the molecular problem and unfortunately in the NaNe case one of them is loosely bound, giving rise to *spurious curve crossings.*[15]

The new method[6,10] we propose overcomes such difficulties by representing the electron-neon interaction by a nonlocal term, consisting of a local potential V_g plus an explicit orthogonality condition between the electron wave function and the orbitals of the neon atom.

The potential $V_g(\vec{r}_g)$ ($\vec{r}_g$ being the distance between the electron and the neon atom) has been fitted in order to reproduce accurate theoretical values for the s-wave phase shifts at very low scattering energies. We used the phase shifts computed by the modified effective range theory of O'Malley,[18] taking for the scattering length the value 0.24 a.u. experimentally determined by Sol, Devos, and Gauthier.[19] The best results were obtained with the following model: The electron-neon interaction is described by the combined effects of a local potential

$$V_g(\vec{r}_g) = -\frac{\alpha d}{2{r_g}^4}\left\{1 - \exp\left[-\left(\frac{r_g}{0.748}\right)^6\right]\right\} - \frac{10}{r_g}\exp[-2.727 r_g]$$

and the orthogonality conditions

$$\int \varphi_{2s}^*(\vec{r})u(\vec{r})d^3r = 0, \qquad \int \varphi_{2p}^*(\vec{r})u(\vec{r})d^3r = 0.$$

The dipole polarizability α_d of the neon atom was taken equal to 2.66 a.u.[20] The orthogonality condition between the electron wave function $u(\vec{r}_g)$ and the neon orbitals φ_{2s} and φ_{2p} (we took the double zeta orbitals of Clementi and Roetti[21]) was achieved by a Lagrange multiplier technique. A deep-lying bound state in the potential V_g is sufficient to ensure the orthogonality to the compact 1s orbital (as in Bottcher's method, this state will lead to an unphysical solution in the molecular problem, but the energy separation from the physical solutions is sufficient to prevent any mixing).

We give in Table I the phase shifts obtained with such a model for the scattering of s, p, and d partial waves. The agreement with the elaborate polarized-orbital calculations of Thompson[22] is excellent for s-wave phase shifts (except at very low energies where the calculations of Thompson are not considered to be accurate) and p-wave phase shifts. The d-wave phase shifts are reproduced to within 10%. A very good agreement exists between Thompson's calculations and the experimental results of Williams and Crowe.[23] The fact that a potential containing only two parameters can reproduce a wide range of scattering data gives a certain credibility to our model.

We then computed the molecular energies by solving the one-electron Schrödinger equation:

$$\left[T + V_g(\vec{r}_g) + V_a(\vec{r}_a) + V_3(\vec{r}_a, \vec{r}_g, R) - \frac{\alpha d}{2R^4}\right]\Psi(\vec{r}_a, \vec{r}_g, R) = E(R)\Psi(\vec{r}_a, \vec{r}_g, R),$$

TABLE I. Phase shifts for low-energy electron scattering.

E	s-wave phase shift δ_0–2π			p-wave phase shift δ_1–π		d-wave phase shift δ_2	
(eV)	MERT[a]	Thompson[b]	This work	Thompson[b]	This work	Thompson[b]	This work
0[c]	0.24	0.17	0.24				
0.034	−0.0183		−0.0184[d]				
0.136	−0.0467	−0.040	−0.0467[d]	+0.004	+0.004		
0.544	−0.123	−0.112	−0.123[d]	+0.009	+0.008		
2.176		−0.302	−0.313	−0.008	−0.009	0.014	0.013
4.896		−0.516	−0.520	−0.074	−0.073	0.036	0.033
8.704		−0.735	−0.727	−0.173	−0.169	0.075	0.066
13.6		−0.946	−0.926	−0.283	−0.275	0.132	0.118

[a] Modified effective-range theory of O'Malley; see Ref. 18.

[b] Polarized-orbitals method of Thompson; see Ref. 22.

[c] Scattering length listed for $E = 0$

[d] Fitted to the MERT results.

where R is the internuclear distance, $\vec{r}_a$ the electron-Na$^+$ distance. The electron-Na$^+$ interaction $V_a(r_a)$ was taken from Klapisch.[24] $V_3(\vec{r}_a, \vec{r}_g, R)$ is a three-body term introduced in the model-potential method by Bottcher and Dalgarno.[25] $\Psi(\vec{r}_a, \vec{r}_g, R)$ is the wave function of the active electron, constrained to be orthogonal to the $2s$ and $2p$ neon orbitals by solving the equation in the appropriate subspace of basis functions. The solution of the Schrödinger equation was determined using a two-center expansion of Ψ on 80 Slater-type orbitals in prolate spheroidal coordinates.[26] Slater atomic orbitals on both atoms appear as a subset. A convergence of 10^{-7} a.u. on the energies of the sodium levels and 10^{-6} a.u. on the molecular energies was obtained. Details of the method will be published elsewhere.[10,15] In addition to the long-range interaction $\alpha_d/2R^4$ between Na$^+$ and Ne included in the Hamiltonian, it is necessary, at short internuclear distances, to introduce the short-range core-core interaction, assumed to be repulsive and exponentially decreasing. The molecular energy is then

$$\mathcal{E}(R)=\mathcal{E}_0(R)+E(R),$$

provided we may approximate the energy of the $X^1\Sigma$ state of the NaNe$^+$ molecular ion by $\mathcal{E}_0(R) - \alpha_d'/2R^4$ and provided the frozen-core model is valid.

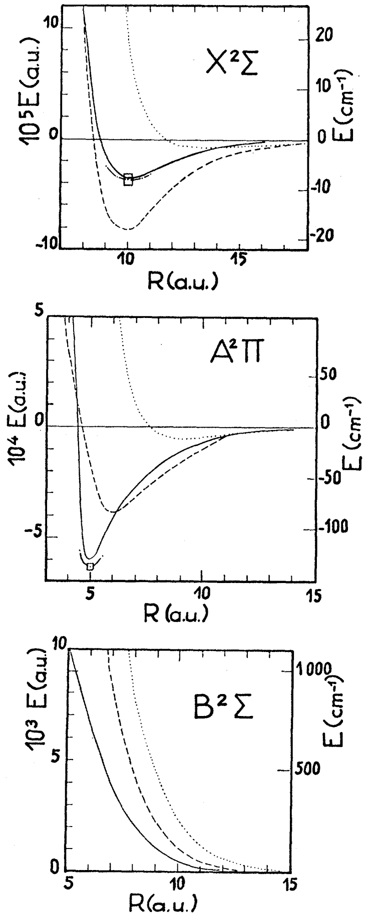

FIG. 1. Potential curves for the $X^2\Sigma$, $A^2\Pi$, and $B^2\Sigma$ states of the NaNe molecule. Solid line, this work. Dash-dotted line, Morse potential fitted to the experimental results of Ahmad-Bitar *et al.*, Ref. 5. The error bars for the well position is indicated. Pseudopotential calculations: dashed lines, Malvern and Peach, Ref. 13; dotted lines, Pascale and Vandeplanque, Ref. 8.

The computed potential curves for the $X^2\Sigma$, $A^2\Pi$, and $B^2\Sigma$ states of the NaNe molecule are given in Fig. 1; the other curves will be published elsewhere.[15] Our result for the position (r_m = 10 a.u.) and the depth (D = 7.8 cm^{-1}) of the well in the $X^2\Sigma$ curve is in excellent agreement with the experimental determination of Ahmad-Bitar *et al.*[5] (r_m = 10.0 ± 0.2 a.u., D = 8.1 ± 1 cm^{-1}). Concerning the well in the $A^2\Pi$ curve, our calculation depends upon the estimation of the core-core repulsion $\mathcal{E}_0(R)$. At shorter internuclear distances ($R < 4$ a.u.) there is a good agreement between both the potentials deduced from scattering experiments,[27] the semiempirical delta-function model of Sondergaard and Mason,[28] the electron-gas model of Kim and Gordon,[29] and the *ab initio* calculations of Gaussorgues.[30] As the experimental determination can be fitted by a formula $A \exp(-BR)$, $\mathcal{E}_0(R)$ can be estimated by extrapolating this expression in the region $R > 4$ a.u. We verify that $\mathcal{E}_0(R)$ becomes negligible for $R > 6$ a.u. A justification for such a model can be found[15] besides in the asymptotic estimation of the exchange interaction of Efremenkova, Radsig, and Smirnov.[31] Choosing for $\mathcal{E}_0(R)$ either the determination of Kita, Noda, and Inouye[27] or of Sondergaard and Mason,[28] we find in both cases for the well depth and position the values D = 132 cm^{-1}, r_m = 5 a.u., which are in very good agreement with the experimental determination (D = 140 ± 3 cm^{-1}, r_m = 5.1 ± 0.1 a.u.) bearing in mind the crudeness of our estimation of $\mathcal{E}_0(R)$.[32]

We have shown that by using a model-potential technique with an explicit orthogonality condition between the sodium valence-electron wave function and the neon ground-state orbitals, we obtain for the NaNe system potential curves that are in excellent agreement with the recent experiment on laser spectroscopy of bound NaNe molecules by Ahmad-Bitar *et al.*[5]

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