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Low-energy scattering of electrons from Li_2

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Calculations of total cross sections for the scattering of low-energy electrons by Li_2 have been performed in the fixed-nuclei approximation. These calculations employed a parameter-free model of the correlation-polarization interaction and an essentially exact treatment of the exchange.

I. INTRODUCTION

Although the structure[1] of the Li_2 molecule has received much experimental and theoretical attention, the polarizabilities[2] have been less extensively studied. On the other hand, only Miller *et al.*[3] have reported electron scattering cross sections for this molecule. Their results show the largest cross section ever observed for a neutral, nonpolar molecule. This observation is not surprising in view of the very large values of the dipole polarizabilities.

We present theoretical results of electron-Li_2 scattering cross sections and explore the validity of a simple model[4] of the correlation-polarization interaction for such highly polarizable molecules. The Li_2 system presents some rather formidable theoretical and computational challenges. First, the wide separation of the Li atoms [$R_{eq}=5.05$ bohr (Ref. 5)] implies that large partial wave expansions of both the bound and continuum wave functions must be employed to guarantee proper convergence of the cross sections. In this sense, electron scattering from Li_2 more closely resembles[6] that from CO_2 than from N_2 or HCl. Second, the large polarizabilities[2] of the molecule indicate that correlation effects will be very important and that the static-exchange model will probably not be appropriate. The complexity of the Li_2 system is further attested to by the sensitivity of the ground and negative-ion potential curves to the basis set and level of treatment.[1] Therefore, scattering from this molecule imposes severe tests for any model. To ensure that the accuracy of the results is limited by the physical approximations and not by the precision of the calculations, all parameters governing convergence were chosen to achieve total cross sections accurate to better than 5%.

II. THE INTERACTION POTENTIAL

The interaction potential consists of static, polarization, and exchange terms. The static potential is the average over the ground-state molecular charge distribution of the electrostatic interaction of the electron and molecule. For elastic scattering, the polarization-correlation contribution accounts for all virtual transitions to excited electronic states. The exchange contribution arises from the enforcement of the Pauli principle on the total system wave function, which consists of an antisymmetric product of the continuum and ground-state bound orbitals. Since both the exchange and polarization terms are nonlocal and energy dependent, they require special treatment.

We obtained a Legendre expansion of the static (S) potential[7] from the electronic charge density[8] generated by a near—Hartree-Fock (HF) wave function. The molecular orbitals were represented by a single-configuration HF wave function composed of a Gaussian-type-orbital (GTO) uncontracted basis[9] of [10s,4p] functions, augmented by one s and one p function with coefficients 0.01 and 0.02, respectively, at the nuclei. The maximum moments used in the Legendre expansion of the static potential were 76 (74) for nuclear and 24 (24) for electronic for gerade (ungerade) symmetries.[10]

The static potential is augmented by a parameter-free model of the correlation-polarization[4] (COP) interaction. This model, which uses the free-electron gas correlation for short distances and the asymptotic form of the polarization, has a simple dependence on the molecular charge density and polarizabilities. The COP potential was also represented by a Legendre expansion in which only the monopole and quadrupole terms that couple to the isotropic and quadrupole polarizabilities were retained. The values of the spherically symmetric and quadrupole static polarizabilities used are 204.737 and 45.411 a.u.,[11] respectively.

We incorporated exchange effects through a separable-potential approximation.[12] In this treatment the exchange operator is represented by a sum of separable terms, represented by a discrete GTO basis. Due to the short-range nature of the exchange kernel, the convergence in the number of separable basis functions is rapid. The set of GTO basis functions used to generate the static potential was also used in the calculations of the separable-potential expansion. Depending on the symmetry of the continuum functions, we added a diffuse GTO set at the midpoint, selected as a geometric progression of ratio 2. For example, for the Σ_g symmetry, this extra set consisted of five s functions with coefficients 0.005, 0.0025, 0.001 25, 0.000 62, and 0.000 31, and five d_{zz} functions with coefficients 0.05, 0.025, 0.0125, 0.006 25, and 0.0031. This interaction potential is denoted ESECOP (exact static-exchange correlation polarization).

Earlier applications of the ESECOP approximation for H_2,[4] N_2,[4] HCl,[13] and HCN (Ref. 14) gave very satisfactory results for total and differential elastic and vibrational cross sections at scattering energies below 1 Ry. In those cases, the short-range part of the model correlation-

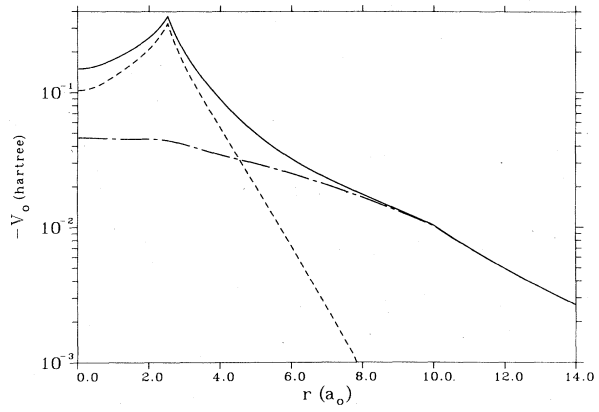

FIG. 1. Spherically symmetric terms in the interaction potential for electron-Li_2 scattering: the static potential (— — —); the correlation-polarization model (—·—·—); sum of the two previous terms (——).

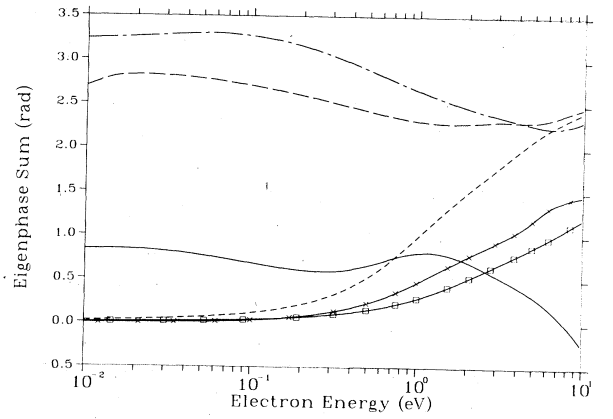

FIG. 3. Eigenphase sums for several scattering symmetries: Σ_g (——); Σ_u (—·—·—); Π_u (—··—··—); Π_g (— — —); Δ_g (×××); Δ_u (□□□).

polarization potential is much weaker than the static potential. For Li_2, the model polarization part represents a much larger contribution to the total potential and, consequently, poses a more stringent test of the theory. For example, for N_2 the contribution to the V_0 static component of the potential near the nuclei is almost 50 times larger than that of the corresponding model[4] correlation-polarization term while for Li_2 the ratio is less than a factor of 8.

Figure 1 shows the spherically symmetric terms in the interaction potential. The contribution of the induced quadrupole polarization term to the potential is not very important, since it is much smaller than the permanent quadrupole term.

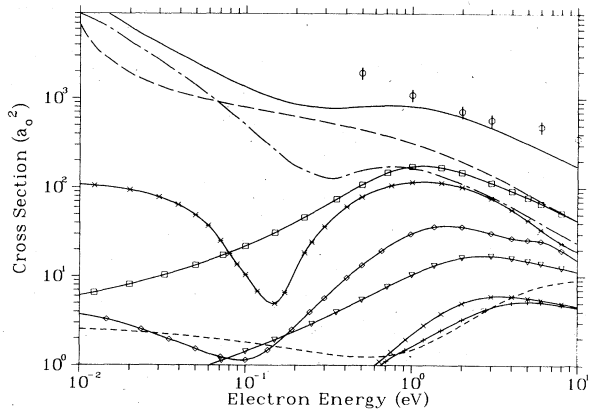

FIG. 2. Cross sections for scattering of electrons by Li_2: partial cross section for Σ_g (—··—); partial cross section for Σ_u (⋇⋇⋇); partial cross section for Π_u (—·—·—); partial cross section for Π_g (□□□); partial cross section for Δ_g (◇◇◇); partial cross section for Δ_u (▽▽▽); partial cross section for ϕ_u (×××); partial cross section for ϕ_g (+ + +); sum of partial cross section for symmetries form $M_L=4$ up to $M_L=38$ (— — —); total cross sections (——); experimental data of Miller *et al.* (Ref. 3) (○○○).

III. SOLUTION OF THE SCATTERING EQUATIONS

The scattering equations are solved using an integral equation formulation[12(c),15] of the close-coupling approximation. All calculations were carried out at the equilibrium internuclear separation [$R_{eq}=5.05$ bohr (Ref. 5)] and in the molecular body-fixed frame within the fixed-nuclei (FN) approximation.[16]

For incident electron energies below 1 eV the scattering equations were solved for eight collisional symmetries: Σ_g and Σ_u ($M_L=0$), Π_g and Π_u ($M_L=1$), Δ_g and Δ_u ($M_L=2$), and ϕ_g and ϕ_u ($M_L=3$). For higher energies, we increased this number to $M_L=7$, at 10 eV. After this point, the close-coupling results were in good agreement with the unitarized-Born[17] approximation values (better than 2%). We are, in this way, justified in completing our calculations, for the entire energy range, by adding the unitarized-Born cross sections for the higher symmetries up to $M_L=38$. The exchange potential was used for only the lower six symmetries from Σ_g to Δ_u. This truncation

TABLE I. Total cross section for electron-Li_2 scattering (in units of a_0^2).

Energy (eV)	Cross section (a_0^2)	Energy (eV)	Cross section (a_0^2)
0.010	1.59(+4)[a]	0.750	8.34(+2)
0.020	6.37(+3)	1.000	8.14(+2)
0.025	5.03(+3)	1.500	7.17(+2)
0.030	4.17(+3)	2.000	6.17(+2)
0.050	2.50(+3)	3.000	4.70(+2)
0.070	1.94(+3)	4.000	3.75(+2)
0.100	1.33(+3)	5.000	3.12(+2)
0.150	9.94(+2)	6.000	2.68(+2)
0.250	8.11(+2)	8.000	2.09(+2)
0.500	8.10(+2)	10.000	1.72(+2)

[a]The numbers in parentheses are the power of 10 by which the cross section should be multiplied.

TABLE II. Σ_g and Π_u eigenphase sums for electron-Li_2 scattering (in radians).

Energy (eV)	Σ_g (rad)	Π_u (rad)	Energy (eV)	Σ_g (rad)	Π_u (rad)
0.010	0.8368	2.6935	0.750	0.7618	2.3545
0.020	0.8349	2.8215	1.000	0.8097	2.3164
0.025	0.8246	2.8207	1.500	0.7893	2.2907
0.030	0.8129	2.8146	2.000	0.7095	2.2958
0.050	0.7661	2.7814	3.000	0.5505	2.3183
0.070	0.7262	2.7454	4.000	0.4295	2.3147
0.100	0.6796	2.7012	5.000	0.3186	2.3131
0.150	0.6288	2.6418	6.000	0.2098	2.3380
0.250	0.5911	2.5549	8.000	−0.0138	2.4154
0.500	0.6618	2.4247	10.000	−0.2361	2.4764

is justified since the exchange interaction is short ranged and since the large partial waves associated with the higher symmetries do not penetrate into this region. The maximum orbital angular momentum quantum number for the expansion of the scattering function in partial wave is 38 for gerade and 37 for ungerade symmetries.

IV. THE CROSS SECTIONS AND THE EIGENPHASE SUMS

The theoretical total cross section (Fig. 2) includes the elastic and rotational contributions and is compared to the experimental results[3] that include elastic, rotational, vibrational, electronically inelastic, and ionization cross sections. The effects of the vibrational contributions will probably be in the range of 10%. Except near resonances, the elastic vibrational cross section $v=0$ to $v'=0$ is usually close to the FN result, and contributions from vibrational excitations are generally smaller by factors of 5 or more. Miller *et al.*[3] estimate that the electron-impact ionization cross sections rises from zero at 5 eV up to 17 or 20 a.u. at 10 eV, incident electron energy. We do not have any estimates of the importance of the electronically inelastic process for Li_2. In the higher energies range, we might expect the contributions of the electronically inelastic cross section to be considerable, as in the case for the electron Li atom scattering.[18] For the atomic scattering a two-state close-coupling calculation shows that the contribution of the $2s$-$2p$ transition increases the total cross sections to more than twice the elastic $2s$-$2s$ part at 10 eV. A final determination of the validity of this observation must, of course, await more elaborate molecular close-coupling calculations.

The results for energies below 1 eV present some minima and maxima in the partial cross sections that could be artifacts of the approximation. Figure 3 shows the eigenphase sums for the six lower symmetries. A Ramsauer-Towsend minimum in the Σ_u cross section at 0.22 eV corresponds to the point the Σ_u eigenphase sum reaches the value of π. The symmetric Π_g presents a very broad resonance around 1 eV. We present in Tables I and II the total cross sections and the eigenphase terms for the Σ_g and Π_u symmetries, in the 0.01—10 eV energy range.

Figures 4 and 5 show the cross sections and eigenphase sums for the symmetries Σ_g and Π_u at very low energies (0.003—0.02 eV). The Π_u symmetry presents a very narrow resonance ($\Gamma=1.7\times10^{-3}$ eV) at $E=6.45\times10^{-3}$ eV. This resonance may have an analog with the very low ^3P

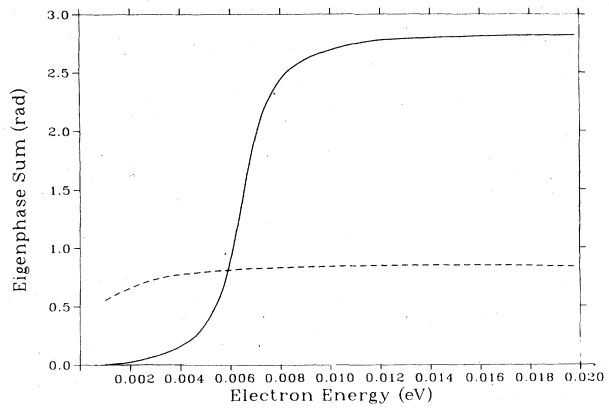

FIG. 4. Eigenphase sums for the Σ_g and Π_u scattering of electrons by Li_2, at very low energies: Σ_g (— — —); Π_u (——).

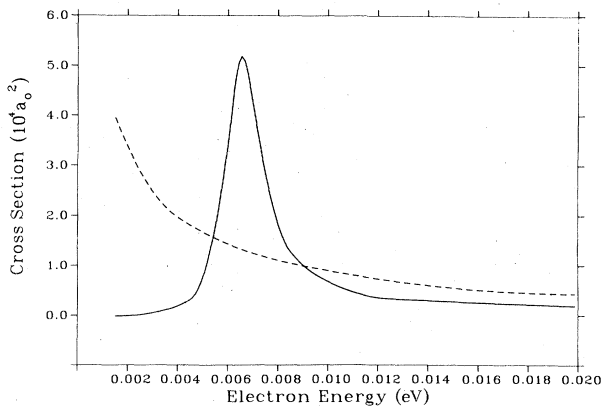

FIG. 5. Partial cross sections for the Σ_g and Π_u scattering of electrons by Li_2, at very low energies. Different symmetries are indicated by the same symbols as Fig. 4.

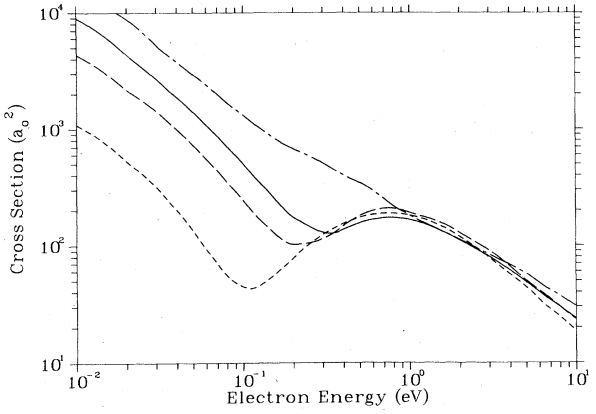

FIG. 6. Partial cross sections for Σ_g elastic scattering of electrons by Li_2: ESECOP results (——); cutoff polarization with $r_c=5.5$ bohr (—·—·—); with $r_c=7.0$ bohr (—·—·—·—); with $r_c=10.0$ bohr (— — —).

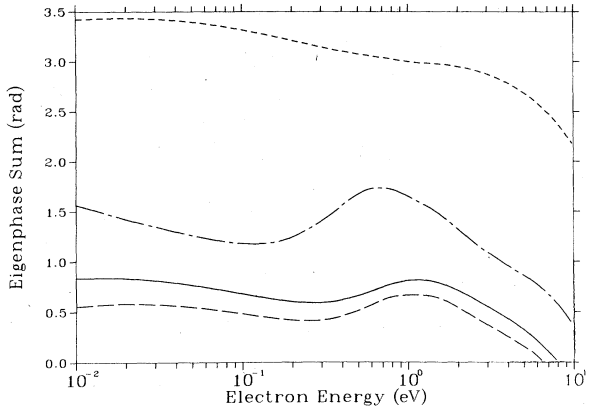

FIG. 8. Eigenphase sums for Σ_g scattering symmetry for the different interaction potentials. Different potentials are indicated by the same symbols as Fig. 6.

resonance for the e-Li atom scattering.[18,19] The Σ_g eigenphase sum indicates a very large scattering length, which is confirmed by the behavior of the cross section curve, and may be indicative of a virtual state. However, the exact positions of the $^2\Sigma_g$ Li_2^- and neutral potential curves are quite sensitive to the models employed. Final confirmation of the precise low-energy results may possibly require more detailed calculations.

V. TESTS OF THE CORRELATION-POTENTIAL MODEL

To test the sensitivity of the results to our potential, we repeated the calculations keeping the static and exchange potentials, but using a cutoff form of the polarization potential.[20] This model uses a local form correct asymptotically, but cutoff at short distances with one adjustable parameter, the cutoff radius r_c

$$V=-\frac{\alpha_0+\alpha_2 p_2(\theta)}{2r^4}(1-e^{-(r/r_c)^6}) . \quad (1)$$

We used three different values of the cutoff radius r_c. We have chosen two of the radii as 5.5 and 10.0 bohr as extremes, the first being just barely larger than the internuclear distance and the second as almost twice this value, lying outside most of the charge distribution of Li_2. The third radius was chosen to be between the two at 7.0 bohr. The test was performed for the symmetries Σ_g and Π_u that presented the largest contributions to the total cross sections for energies below 1 eV (Figs. 6 and 7). The cross sections in this energy range are extremely sensitive to the cutoff radius of the potential. Figures 8 and 9 show the eigenphase sums for these symmetries. Due to the sensitivity encountered we find it difficult to assess the validity of the model in the low-energy range (below 1 eV). Furthermore, preliminary optical potential results show con-

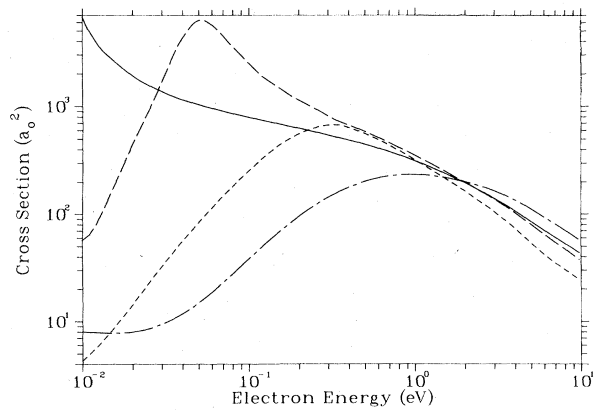

FIG. 7. As Fig. 5 for Π_u symmetry.

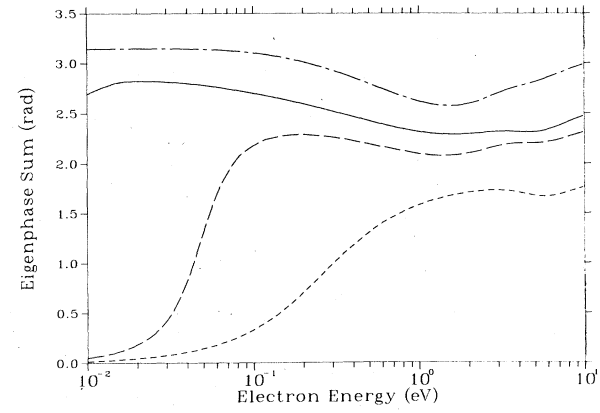

FIG. 9. As Fig. 8 for Π_u symmetry.

siderable sensitivity to the choice of the basis in this region.[11]

The cross sections are much less sensitive to the model for energies above 1 eV, all being within a factor of 2. This factor confirms our belief that the results are reasonable in this energy range even though this approximation is very crude and can cause errors beyond those coming from the value of r_c.[21]

VI. FINAL REMARKS

We present theoretical total cross section for electron-Li_2 scattering in the fixed-nuclei approximation employing an exact treatment of the static and exchange interactions and a model potential, based on a free-electron gas approximation, to represent the correlation-polarization contributions. In the intermediate energy regime (1—5 eV), the results are in reasonable agreement with the experiments of Miller *et al.*[3] For higher energies, the agreement is not as good due, probably, to the opening of inelastic electronic channels, which are not included in our model. At low energies (<1 eV) the cross sections are sensitive to the model polarization as was demonstrated by considering several cutoff forms. In this energy range, future experimental results or more detailed calculations should provide an ideal test for our approximations.

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