

Polarization effects in low-energy electron scattering from silane molecules in an exact static-exchange model

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We have investigated the effects of various model polarization potentials in low-energy (below 15 eV) electron-SiH₄ collisions in which electron-exchange correlation is treated exactly via an iterative procedure. Two models of the parameter-free polarization potential are employed; one, the $V_{\text{pol}}^{\text{JT}}$ potential, introduced by Jain and Thompson [J. Phys. B **15**, L631 (1982)], is based on the polarized-orbital theory; the other, the correlation-polarization potential $V_{\text{pol}}^{\text{CP}}$, first proposed by O'Connell and Lane [Phys. Rev. A **27**, 1893 (1983)], is given as a density functional. In this low-energy region, the differential as well as integral cross sections are greatly influenced by such short-range-correlation and long-range-polarization interactions. We found that a local parameter-free model to mimic charge-distortion effects is quite successful if it is determined under the polarized-orbital-type approach rather than based on density-functional theory.

It is only recently that electron-exchange correlation in low-energy electron scattering with nonlinear polyatomic molecules can be treated exactly [1–10]. A complete calculation treating both the exchange and polarization effects exactly is still an open problem. It is well known that low-energy ($E \leq 15$ eV) electron-molecule collision dynamics depends strongly on approximations involved in the treatment of exchange and polarization correlations [3,11]. From a first-principles point of view, these effects are nonlocal and energy dependent. If the total wave function of the electron-molecule complex is expanded as

$$\Psi_T = A \sum_i \Phi_i(r_1, r_2, \dots, r_N; \mathbf{R}) F_i(r_{N+1}) + \sum_{\alpha} c_{\alpha} \Phi_{\alpha}(r_1, r_2, \dots, r_{N+1}), \quad (1)$$

then both the short-range- and long-range-correlation effects are intrinsically included exactly in a natural way. In Eq. (1), Φ_i is the i th electronic state of the N -electron target in a fixed-nuclei approximation, F_i is the corresponding continuum function, and A is the usual antisymmetrization operator which gives rise to nonlocal exchange correlation. The expansion over the target states Φ_i also includes some pseudostates to represent target polarizability and the second term in Eq. (1) describes the $(N+1)$ -electron correlation functions. It is a formidable task to use expansion (1) as such even for the simplest target H₂. The easiest way is to work in a single-state [$i=1$ in Eq. (1)] approximation and neglect the second term altogether. This is the so-called static-exchange (SE) approximation. Assuming that we are concerned here with electronically elastic scattering only, the effects due to electronically (virtual) excited states and the correlation term in (1) can be approximated via a local term known as the polarization potential. Even in this simplified SE-plus-polarization (to be denoted as SEP) model, the calculations on the nonlinear polyatomic systems are very difficult and require a set of computer

programs different from those used for linear molecules. Consequently, very little theoretical work has been done on electron scattering from polyatomic molecules. Most of the earlier work on electron-polyatomic-molecule collisions employed model potentials for both the exchange and polarization interactions (see Ref. [3]).

It is now a well-established fact that in the low-energy regime, the use of model potentials for both the exchange and polarization forces is rather misleading due to the fact that, in order to make theory and experiment closer these interactions do compensate for each other. A computationally simplified approach is one where exchange is treated exactly while the polarization is included via an approximate local model potential [3–7]. This scheme has been very recently employed to investigate near-threshold vibrational excitation in the case of e -H₂ collisions [12]. It therefore becomes quite important to employ a better model for polarization effects. In this respect a parameter-free potential determined from an actual distorted target in the presence of an incoming projectile should be a desired choice. In the past, two such prescriptions for nonadjustable model polarization potentials have been suggested for electron-polyatomic-molecule collisions in general: these are the $V_{\text{pol}}^{\text{JT}}$ (Jain and Thompson [13]) and $V_{\text{pol}}^{\text{CP}}$ (Gianturco, Jain and Pantano [14]; CP denotes correlation polarization) (for description see below).

In the following the SEP(JT) model means the use of $V_{\text{pol}}^{\text{JT}}$ (JT for Jain and Thompson [13]) along with our iterative static exact-exchange (SEE) approach, while the SEP (CP) employs the $V_{\text{pol}}^{\text{CP}}$ parameter-free forms. In a recent paper [5] on the e -CH₄ system, we demonstrated that (i) the differential cross sections (DCS) and the Ramsauer-Townsend (RT) effect are very sensitive to the approximations involved in the calculation of the polarization potential and (ii) the SEP(JT) model was better than the SEP(CP) one. The $V_{\text{pol}}^{\text{JT}}$ potential was obtained by Jain and Thompson [13] from the second-order energy of the molecule evaluated from the first-order wave func-

tion Φ_1 of the target; Φ_1 was determined following the method of Pople and Schofield [15], using an expansion in terms of the ground-state wave function Φ_0 with the expansion coefficients obtained variationally. In order to correct for the nonadiabatic effects in the target region, Jain and Thompson [13] borrowed the nonpenetrating criterion of Temkin [16]. On the other hand, the $V_{\text{pol}}^{\text{CP}}$ potential is based on the hybridization of the short-range correlation energy of the target and the long-range-polarization form $(-\alpha_0/2r^4)$, where α_0 is the polarizability of the target in atomic units. The $V_{\text{pol}}^{\text{CP}}$ potential was first proposed by O'Connell and Lane [17] for atomic targets and later modified for molecular targets by Padial and Norcross [18]. It is much easier to evaluate the $V_{\text{pol}}^{\text{CP}}$ potential than the corresponding $V_{\text{pol}}^{\text{JT}}$ term.

A comparison of the present nonadjustable and energy-independent $V_{\text{pol}}^{\text{JT}}$ and $V_{\text{pol}}^{\text{CP}}$ potentials is given in Fig. 1. We see that the $V_{\text{pol}}^{\text{JT}}$ model is stronger than the $V_{\text{pol}}^{\text{CP}}$ potential in the 0.5–4-a.u. radial region. In addition, near the origin, the $V_{\text{pol}}^{\text{JT}}$ has the correct form. It was observed by Jain and Thompson [19] that when the $V_{\text{pol}}^{\text{JT}}$ approximation is employed along with free-electron-gas exchange along with orthogonalization procedure [20] (OFEGE) model, the position of the RT minimum occurs at much lower energy (0.08 eV compared to the experimental value around 0.25 eV); this indicates that the $V_{\text{pol}}^{\text{JT}}$ is a weak potential when employed along with the OFEGE model [19]. Gianturco, Pantano, and Scialla [21] employed the $V_{\text{pol}}^{\text{CP}}$ along with model exchange (in their so-called modified semiclassical-exchange) potential. Yuan [22] has included exchange effects exactly in a spherical approximation, which is not appropriate in this low-energy region. It will therefore be very interesting to compare these polarization models in an exact static exchange calculation. The purpose of the present work is to draw some useful conclusions regarding such a comparison.

The theory and cross-section formulas have already been described in a recent paper [7]. In brief, we solve the following integro-differential scattering equation in

the body-fixed (BF) frame of reference under the single-center scheme,

$$\left(-\frac{1}{2}\nabla_r^2 + V_{\text{st}} + V_{\text{pol}} - \frac{1}{2}k^2\right)F(\mathbf{r}) = \sum_{\alpha} \int \phi_{\alpha}^*(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1}F(\mathbf{r}')d\mathbf{r}'\phi_{\alpha}(\mathbf{r}), \quad (2)$$

where k^2 is the electron energy in atomic units, V_{st} is the static potential, and ϕ_{α} represents a bound orbital. Equation (2) was solved separately for each symmetry (A_1 , A_2 , E , T_1 , and T_2) and energy. In the single-center expansion of the potential and continuum function, we included terms up to $l=6$, which defines the size of the \mathbf{K} matrix of a given symmetry. In this low-energy region (below 1 eV), the convergence with respect to various single-center expansions is almost perfect.

There have been several experimental studies on the e - SiH_4 system [23–32] including work on the total differential, and momentum-transfer cross sections. For a full list of references on the e - SiH_4 collisions, experimental or theoretical, refer to our recent paper [7]. First we discuss our total (rotationally summed but vibrationally and electronically elastic) and momentum-transfer cross sections in the present energy region.

Figure 2 displays our σ_t values in both the SEP(JT) (solid line) and SEP(CP) (lower dashed curve) models along with the experimental data of Wan, Moore, and Tossell [23] (crosses). Also shown in this figure are our SEE results (multiplied by a factor of 3) without polarization (upper dashed curve). No other close-coupling calculations where exchange is treated exactly are available below 1 eV. It is also worth mentioning that polarization effects are more crucial below 1 eV than above this energy. We see from Fig. 2 that the SEE cross sections without polarization effects are too large. It is clear from Fig. 2 that the SEP(JT) curve, predicting a RT structure around 0.25 eV, is more favorable. Although the measured values of Wan, Moore, and Tossell do not seem to show any RT minimum, its existence is clearly visible in their σ_t curve around the same energy, 0.25 eV (see Fig. 5 of Ref. [23]). The existence of the RT minimum is also

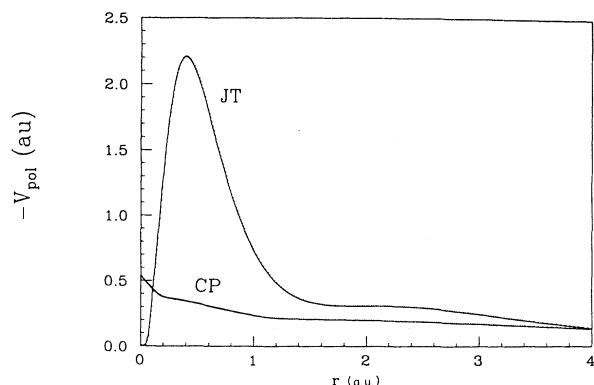


FIG. 1. Nonadjustable polarization potentials for the e - SiH_4 system in the JT and CP approximations as a function of radial distance r in atomic units. Note that each potential is multiplied by a factor of $\sqrt{4\pi}$. For notations see the text.

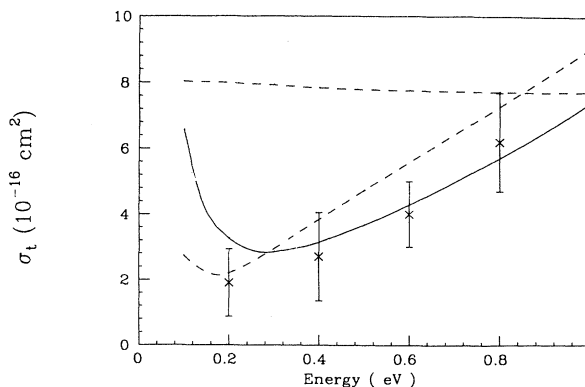


FIG. 2. Total cross sections for the e - SiH_4 elastic collisions below 1 eV. Theory: solid line, present SEP(JT) model; dashed line, present SEP(CP) model. The upper dashed curve represents the static exact exchange (SEE) (without polarization). Experiment: crosses, Wan, Moore, and Tossell [23].

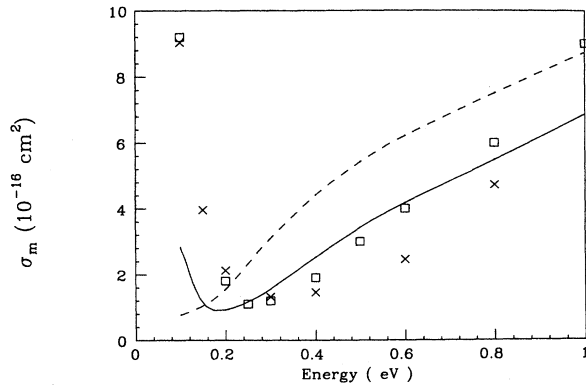


FIG. 3. Momentum-transfer cross sections for the e - SiH_4 system in the present SEP(JT) (solid curve) and SEP(CP) (dashed curve) models. The swarm data are taken from Refs. [29] (crosses) and [30] (squares).

confirmed in swarm-type studies by several investigators [28–32]. We now discuss our σ_m cross sections below 1 eV.

Figure 3 illustrates our σ_m results in both the SEP(JT) and SEP(CP) models along with swarm data [29,30]. The experimental σ_m cross sections (Fig. 3) exhibit the RT minimum around 0.25 eV, while our SEP(JT) (solid line) predicts this minimum around 0.2 eV. The SEP(CP) σ_m results (dashed curve in Fig. 3) do not show any RT effect. In the σ_t curves of Fig. 2, the corresponding positions of the RT minimum in SEP(JT) and SEP(CP) models occur, respectively, at 0.16 and 0.25 eV. In general, the minimum in σ_m occurs at lower energy than the corresponding minimum in the σ_t cross sections. Even the

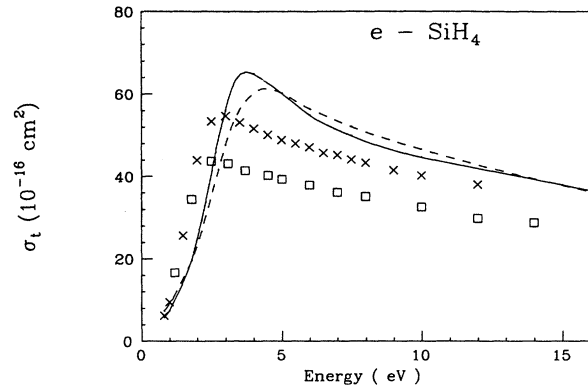


FIG. 4. Same as in Fig. 2 except in the 1–15-eV range. The experimental points are from Refs. [23] (crosses) and [27] (squares).

magnitude of σ_m results in the SEP(JT) model agrees very well with the swarm results (Fig. 3). On the other hand, the SEP(CP) σ_m are not in agreement even qualitatively with the measured values.

In Fig. 4, we have shown our σ_t values at 1–15 eV for both models, along with measured data. Again we see that the SEP(JT) model is superior to the SEP(CP) one. In particular, the position of the shape-resonance in the SEP(JT) case is in better agreement with the experiment as compared to the SEP(CP) model. The discrepancy between experimental data and present SEP(JT) calculations suggests that a realistic polarization potential may be even stronger than the present JT approximation. A full polarized-orbital-type calculation is required in order

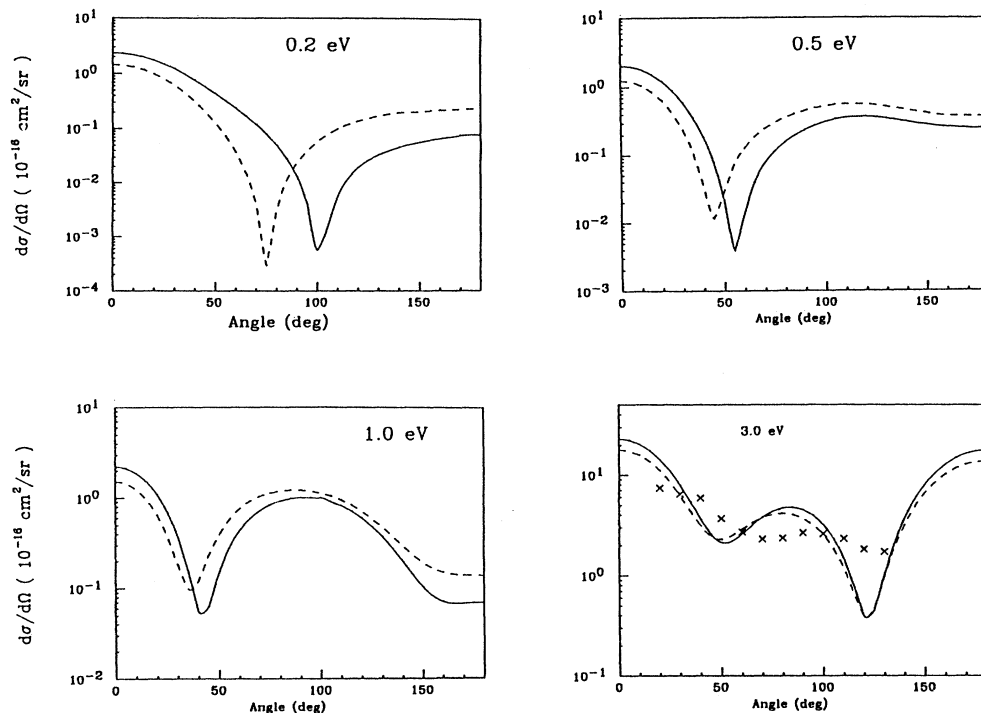


FIG. 5. Elastic differential cross sections for the e - CH_4 scattering at 0.2, 0.5, 1, and 3 eV. Theory: solid curve, present SEP(JT) model; dashed line, present SEP(CP) model. At 3 eV, the measured values of Tanaka *et al.* [32] are shown by crosses.

to test this hypothesis.

The DCS's present a more stringent test of any theoretical model when compared with experiment. The two models SEP(JT) and SEP(CP) differ significantly when compared at the DCS level. Figure 5 displays the angular functions at 0.2, 0.5, 1, and 3 eV in both models along with experimental data (only at 3 eV). There is no experimental data at or below 1 eV. The DCS's at 0.2 and 0.5 eV in Fig. 5 present distinct features. At 0.2 eV, the dip in the case of the SEP(JT) model occurs at 100° , as compared to 75° in the SEP(CP) case. This difference of 25° in the positions of minima in the DCS at 0.2 eV reflects the sensitivity of low-energy scattering with respect to polarization effects. It will be interesting to see experimental data at this energy. At 0.5 eV (Fig. 5), the difference in the positions of the minima in both the models is about 10° . Note that in case of e -CH₄ scattering [5] a similar distinction is observed at 0.5 eV between the SEP(JT) and SEP(CP) models. The experimental DCS at 0.5 eV for e -CH₄ scattering agrees with the SEP(JT) model. We therefore expect that our SEP(JT) curve (in Fig. 5 at 0.2 and 0.5 eV) is more realistic and reliable than the corresponding data in the SEP(CP) model. At 1 eV (Fig. 5), there is still some difference between the two models, however, the qualitative features are quite similar. We emphasize here that the significant discrepancy between the two polarization potentials is to be found below 1 eV.

Let us examine our higher-energy DCS where experimental data are available for comparison. At 3 eV (Fig. 5), both the theoretical models predict similar dip struc-

ture, while significant difference is seen in the forward and backward directions. We can see from the 3-eV DCS that the SEP(JT) potential is stronger than that of the SEP(CP) model. Both the models have considerable discrepancy with the experimental DCS [32]. One reason for this discrepancy may be the inadequacy of present polarization models. On the other hand, the accuracy of measured data is not clear since no other experimental studies are available at this time.

Finally, our SEP(JT) model appears to be better than the SEP(CP) model, in particular in the RT-minimum region. This conclusion is consistent with our similar investigation of the e -CH₄ system [5]. However, this conclusion awaits the support of differential measurements for the e -SiH₄ case. There is plenty of room to improve upon the $V_{\text{pol}}^{\text{JT}}$ potential by actually carrying out a full polarized-orbital calculation for the e -SiH₄ system. Our present JT potential is obtained by employing a less accurate method of Pople and Shofield [15], in which all the orbitals are distorted equally. Nevertheless, by employing a better JT-type polarization potential the basic conclusions of this paper will remain valid. It would be quite interesting if more experiments are performed on the DCS quantities, particularly below 3 eV.

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