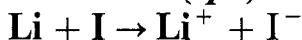


A probe of dynamical models using functional sensitivity densities with application to



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Summary. The functional sensitivity densities $\delta \ln \sigma_{12}(E)/\delta \ln V_{ii}(R)$ for $\text{He}^+ + \text{Ne}(2p^6) \rightarrow \text{He}^+ + \text{Ne}(2p^53s)$ reveal that the collisional excitation cross section $\sigma_{12}(E)$ is insensitive to the additional diabatic curve V_{33} included in some models. The negligible sensitivity of $\sigma_{12}(E)$ to V_{33} offers a quantitative validation of the more popular two state model for collisional excitation of Ne by He^+ . The sensitivity profiles for the collisional ionization $\text{Li} + \text{I} \rightarrow \text{Li}^+ + \text{I}^-$ modeled by crossing diabatic curves V_{11} (covalent) and V_{22} (ionic) shows that the ionization cross section does not depend on inner crossings even when these stem from large distortions in the underlying potential energy curves. The lack of sensitivity to inner crossings establishes the predominant role of the outermost crossing in triggering nonadiabatic transitions.

Key words: Functional sensitivity densities – Nonadiabatic collisions – Diabatic potential energy curves

1 Introduction

A fully quantal treatment of nonadiabatic collisions requires accurate evaluation of more than one electronic curve/surface and the corresponding nonadiabatic coupling matrix elements between the electronic states at a sufficiently large number of representative points on these curves/surfaces [1]. The formidable difficulties inherent in the calculation of curves/surfaces and the corresponding nonadiabatic matrix elements typically has led to the modeling of most nonadiabatic collisions using two crossing diabatic curves V_{11} and V_{22} and an approximate coupling matrix element V_{12} [2]. While two state single crossing models are the most

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common, inclusion of a third state and multiple crossings to permit excitation/quenching [3, 4] has also been explored, e.g., for the collisional excitation $\text{He}^+ + \text{Ne}(2p^6) \rightarrow \text{He}^+ + \text{Ne}(2p^53s)$ both two state [5] and three state [6] models are prevalent.

The functional sensitivity densities $\delta \ln \sigma_{n \rightarrow n'} / \delta \ln V_{ij}(R)$ offer a ready assessment of the importance of the features in the potential curve/coupling matrix element $V_{ij}(R)$ at point R . The sensitivity densities of the collisional transition from state n to n' at total energy E have been utilized to probe the region of potential significance and to decipher the comparative importance of the electronic states involved in the nonadiabatic collisions [7–11]. Those states with only a marginal role may then be deleted from the dynamical model without significant loss of accuracy. When there are multiple crossings, the role of individual crossings in the model curves can be easily probed by examining the sensitivity profiles near each of the crossing points.

The collisional excitation of Ne by He^+ has been modeled by crossing of both two and three diabatic curves. A pertinent question here is the role of the additional curve V_{33} in the collisional excitation of Ne by He^+ . The collisional ionization of Li by I has been modeled using two states [12] with parameters which permit multiple crossings. Although it is expected that nonadiabaticity is controlled by the outermost crossing, it is not obvious whether the inner crossings and other features should have a role in the collisional outcome. The purpose of this communication is to explore the role of the states and the couplings in these two systems.

The methodology and computational considerations in the calculation of functional sensitivity densities have been detailed previously [7–11] and we limit ourselves in the following section to only a short discussion of the results from the two systems of interest. A brief appraisal of the effectiveness of the sensitivity densities in authentication of the underlying dynamical models concludes this paper.

2 Results and discussion

The collisional excitation of Ne by He^+ has been modeled using both a two and a three state model [5, 6]. The two state model is more common and we have analyzed it in some detail previously [8]. The effectiveness of this model *vis-à-vis* the one that includes an extra state V_{33} may be easily ascertained by comparing $\delta \ln \sigma_{12}(E) / \delta \ln V_{ii}(R)$ for the three curves V_{11} , V_{22} and V_{33} . The parametrization of the diabatic curves and couplings is that due to Cho and Eu [6]

$$V_{11}(R) = 21.1R^{-1} \exp(-R/0.678), \quad (1)$$

$$V_{22}(R) = (21.1R^{-1} - 12.1)\exp(-R/0.678) + 0.6174, \quad (2)$$

$$V_{33}(R) = (21.1R^{-1} - 8.2)\exp(-R/0.678) + 0.6212, \quad (3)$$

$$V_{12}(R) = 0.170 \exp(-R/0.667), \quad (4)$$

$$V_{13}(R) = 0.222 \exp(-R/0.667), \quad (5)$$

$$V_{23} = 0 \quad (6)$$

and the three diabatic potential curves are plotted in Fig. 1a. As seen from Eqs. (4) and (5) the coupling between states 1 and 3 is just as strong as that between states

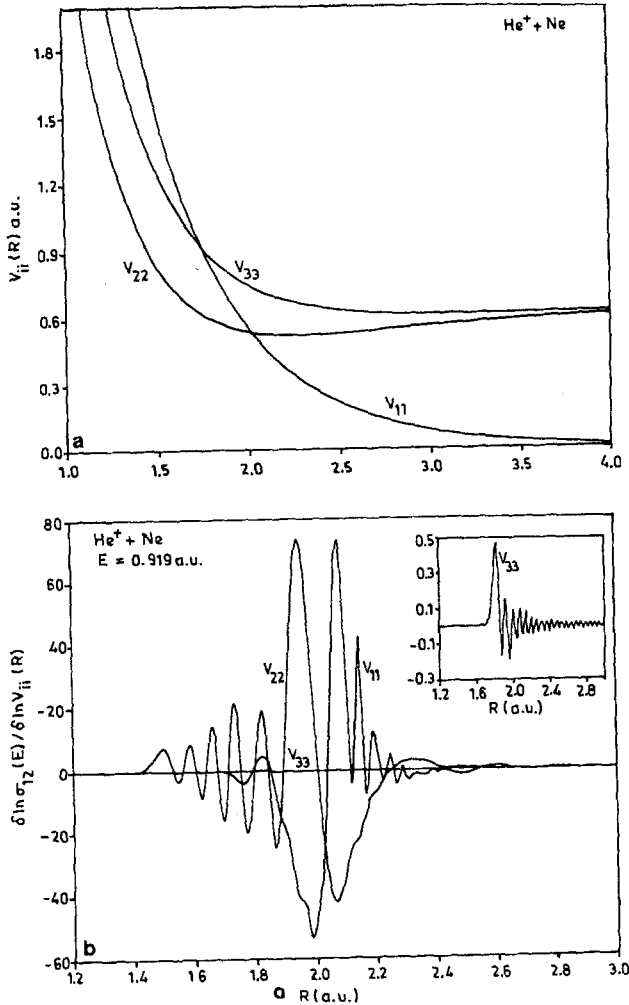


Fig. 1a. The diabatic potentials $V_{11}(R)$, $V_{22}(R)$ and $V_{33}(R)$ for collisional excitation of Ne by He^+ . **b** Log normalized sensitivity profiles $\delta \ln \sigma_{12}(E) / \delta \ln V_{11}(R)$, $\delta \ln \sigma_{12}(E) / \delta \ln V_{22}(R)$ and $\delta \ln \sigma_{12}(E) / \delta \ln V_{33}(R)$ for $\text{He}^+ + \text{Ne}$. The magnitude of the sensitivity to V_{33} (magnified in the inset) is negligible in comparison to that for V_{11} and V_{22} and the sensitivity profiles clearly demonstrate that the curve V_{33} may be deleted from the model. The features in $\delta \ln \sigma_{12}(E) / \delta \ln V_{11}(R)$ and $\delta \ln \sigma_{12}(E) / \delta \ln V_{22}(R)$ are identical to those in our earlier work employing only V_{11} and V_{22} [8]

1 and 2 and at total collisional energies which permit the sampling of the curve crossing region between states 1 and 3 there is no *a priori* reason to expect that the collision cross section σ_{12} will not be sensitive to features in the potential curve V_{33} .

The validity of the restrictive yet more popular two state model [5] may be assessed quantitatively by examining the sensitivity profiles displayed in Fig. 1b. The individual features of the sensitivity profiles $\delta \ln \sigma_{12}(E) / \delta \ln V_{11}(R)$ and $\delta \ln \sigma_{12}(E) / \delta \ln V_{22}(R)$ are identical to those obtained with the two state model

and have been discussed earlier [6]. The comparison of sensitivity densities for V_{11} and V_{22} with that for V_{33} clearly demonstrates the superfluous nature of the additional electronic state V_{33} . The total collisional energy $E = 0.919$ a.u. is the one for which largest sensitivity was seen in our previous studies [6] and while the sensitivity profiles have been presented for this single value of E , essentially same results persist at higher E values. The value of the $\sigma_{12}(E)$ in the three state model at $E = 0.919$ a.u. is 0.7582 (a.u.)² and that from the two state model without V_{33} is 0.7584 (a.u.)². The effectiveness of the two state model is therefore corroborated by the functional sensitivity densities which generally suggest that a small functional change in V_{33} will have nearly a 100-fold less impact on σ_{12} compared to that from a similar change in V_{11} or V_{22} . A similar 100-fold smaller sensitivity to V_{13} in comparison to that for V_{12} has also been seen in all our calculations for this system. These results and those of $\text{Li} + \text{I} \rightarrow \text{Li}^+ + \text{I}^-$ show that the outermost crossings dominantly determine the cross section in these cases under the conditions investigated here.

The collisional ionization $\text{Li} + \text{I} \rightarrow \text{Li}^+ + \text{I}^-$ has been studied by Faist and Levine [12]. The calculations employ two diabatic curves V_{11} and V_{22} for the covalent and ionic states, respectively, where

$$V_{11}(R) = [\text{Acov} + (2.996/R)^2] \exp(-R/0.44) - 1191.2/R^6, \quad (7)$$

$$V_{22}(R) = [1052 + (1.839/R)^8] \exp(-R/0.3786) - (e^2/R), \\ - (6.839e^2/2R^4) - 0.823/R^6 - (2e^2 \times 0.029 \times 6.431)/R^7 + 2.326 \quad (8)$$

and there is an exponentially decaying coupling matrix element $V_{12}(R) = 17.08 \exp(-R/1.239)$ between these two states. The covalent curve V_{11} depends upon a parameter Acov . The collisional cross section σ_{12} is known to be insensitive to variations in the parameter Acov [12] even when the changes in Acov (Eq. (1)) may alter the curves radically and can lead to multiple crossings as seen in Figs. 2a-c. The corresponding functional sensitivity densities are portrayed in Figs. 2d-f. The collisional energies for both these systems are those for which maximum sensitivity was seen in our earlier investigation of $\text{Na} + \text{I}$ [8]. The sensitivity profiles once again demonstrate the greater importance of the ionic curve in comparison to the covalent curve for the collisional ionization of Li by I . The features are identical to those seen for $\text{Na} + \text{I}$ in our earlier work and the span of R values has been clipped as before [8] to exclude the highly oscillatory feature at small R . Here, this clipping leads to the exclusion of R -values where internal crossings take place in Fig. 2a, b. This shortcoming is rectified in Fig. 2g where the unnormalized sensitivity profile $\delta\sigma_{12}(E)/\delta V_{11}(R)$ clearly demonstrates that only the outermost crossing is critical to the nonadiabatic transition. Though the results presented are for a single total energy, the same features persist for other E values as well.

The lack of sensitivity to inner crossings in $\text{Li} + \text{I}$ and to the additional curve V_{33} for $\text{He}^+ + \text{Ne}$ seems to imply that the total inelastic cross section alone is not a sufficiently exacting probe of the individual potential components and an attempt to understand this is desirable. The total inelastic cross section may be analyzed [8] in terms of partial cross sections σ^l where $\sigma_{12}(E) = \sum_{l=0}^{\infty} \sigma^l(E)$ and the angular momentum (l^*) for which there is a maximum in the partial cross-section profile correlates quite well with $l^* = kR^*$, where R^* is the crossing point. While the inner crossings in $\text{Li} + \text{I}$ do manifest themselves in the partial cross-section profiles at near threshold energies, the small R characterizing these inner crossings translate

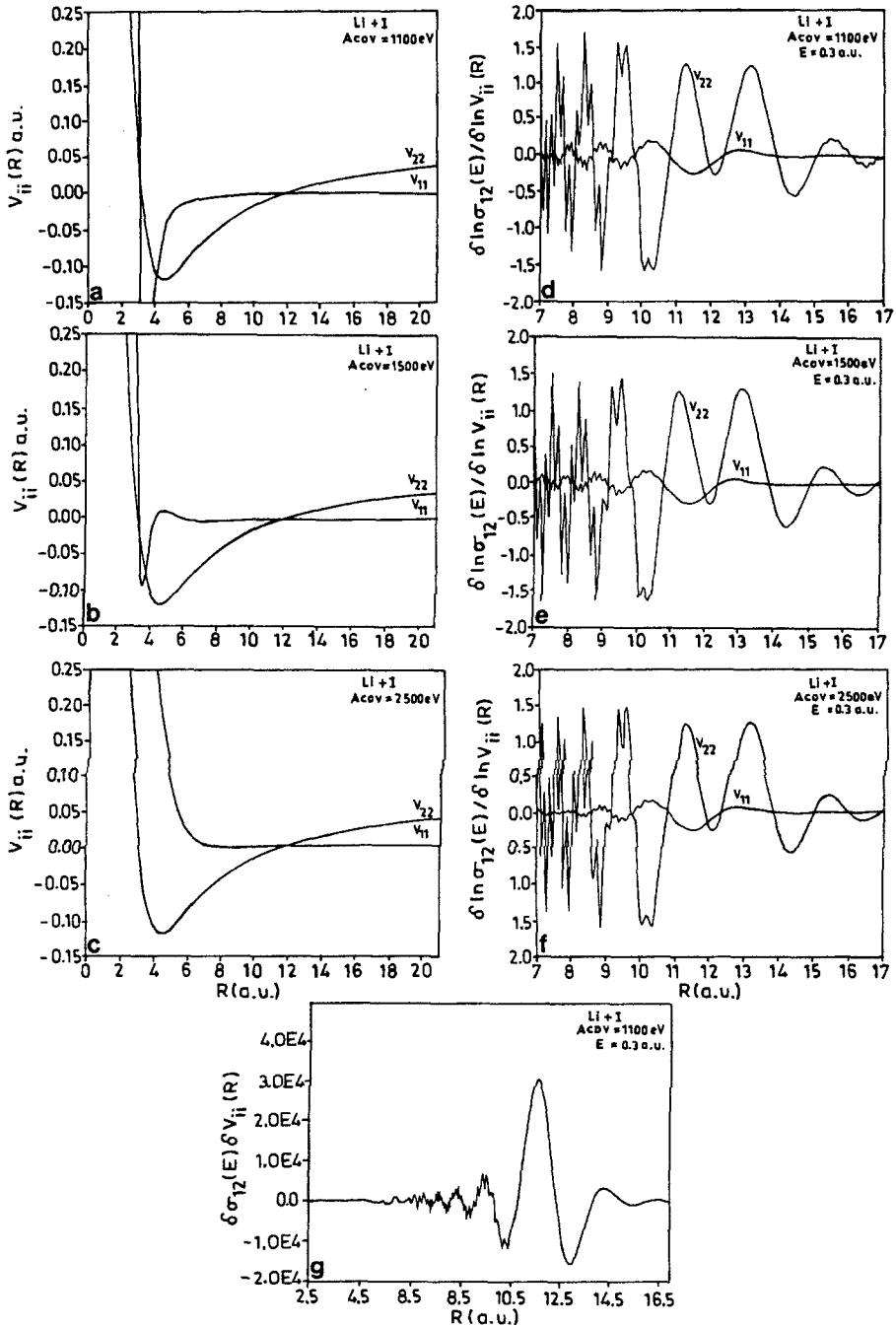


Fig. 2. Diabatic potential energy curves for Li + I for different values of Acov (a–c). The corresponding functional sensitivity densities are displayed in d–g. The sensitivity profiles establish the predominant role of the outermost crossing in controlling the nonadiabatic transitions

into small l contributions which are negligible compared to those from the outermost crossings due to the higher multiplicity of the large l states. At the energies considered here, the effect of the inner crossings cannot be resolved in the partial cross-section profiles and to see their impact we have examined the differential cross sections. The differential cross-section sensitivities do reveal some difference in their highly oscillatory nature at small R but this structure is averaged out upon angular integration to recover the total cross section.

In the three state model of the collisional excitation of Ne by He^+ , the additional curve V_{33} crosses only V_{11} and is not coupled to V_{22} in any way. Furthermore, since the crossing between V_{11} and V_{33} is interior to that between V_{11} and V_{22} , any effect of the V_{33} curve can be seen only at smaller R values and therefore for smaller and less significant l values. At the comparatively large energies required for the excitation of Ne (excitation threshold = 16.8 eV), the impact of the additional curve V_{33} does not translate into any noticeable feature in the partial cross-section profiles for the $\text{He}^+ + \text{Ne}$ system. The differential cross-section sensitivities for the three state model do show some new undulations but there is little impact on the dominant features of the differential cross-section sensitivities from the two state model which remain unaffected.

3 Concluding remarks

A simple intuitive examination of Fig. 1a and the coupling strengths V_{12} and V_{13} in Eqs. (4) and (5) offers no *a priori* reason as to why there should be no role for the diabatic curve V_{33} in the collisional excitation of Ne by He^+ , specially since the collisional energy E is higher than the energy at which V_{11} and V_{33} cross each other. Similarly, there is no obvious reason why the new feature like wells in V_{11} and additional internal crossings (Fig. 2a, b) should have no role in the determination of collisional ionization cross section $\sigma_{12}(E)$ for $\text{Li} + \text{I}$ even though it is clear that final nonadiabaticity has to be determined by the outermost crossing. An economic quantitative probe of these concerns is offered by the sensitivity profiles for these systems.

The partial cross sections and the differential cross sections are somewhat more sensitive to changes in the underlying potential components but the full deconvolution of the impact of additional curves and features probably requires an examination of not only inelastic cross sections but the elastic cross sections as well.

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