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# Interaction Potential between Li+ and HD: Region for Rotational Excitation Cross Sections

**Abstract:** The interaction potential between $Li^+$ and HD (with internuclear separation fixed at 1.4 a.u.) was determined by two different methods using the results of a recent self-consistent-field calculation of the potential energy surface for $Li^+$-$H_2$. In one method, $Li^+$-HD interaction energies were obtained utilizing an analytical representation of the $Li^+$-$H_2$ surface. The second method used *ab initio* $Li^+$-$H_2$ interaction energies directly to yield the $Li^+$-HD potential surface by means of interpolation procedures. The interaction potentials determined by the two methods are essentially identical and have been fit to an analytical form, $V(r, \theta) = \sum_l v_l(r) P_l (\cos \theta)$, to facilitate scattering studies. For large center of mass distances, perturbation theory is in good accord with the potentials constructed by the two procedures.

## Introduction

Accurate interaction potentials are essential for a detailed understanding of internal (rotational, vibrational) energy transfer. They are necessary for reliable interpretation of experimental results and provide unique input to theoretical calculations of cross sections of the mutual effect of the scattered systems.

Recent advances [1] in the molecular beam scattering method [2] and in fluorescence spectroscopy [3] are beginning to yield cross sections for internal energy exchange between known initial and final states. Such data are of fundamental significance since they can serve as tests of the accuracy of interaction potentials and methods for the computation of cross sections.

Recent time of flight experiments with monoenergetic beams of $K^+$ [2(e), 2(f)] and $Li^+$ [2(c), 2(d), 2(i)] incident on $H_2$ and $D_2$ have yielded the first results on the energy dependence in the center of mass frame of the energy transferred to internal degrees of freedom. Because of the apparatus arrangement, these findings relate almost exclusively to vibrational excitation. To assist the interpretation of the $Li^+$ experiments, quantum-mechanical potential energy surface calculations have recently been reported [4,5] and cross-section calculations are in progress [6,7] using these *ab initio* surfaces. Although information on rotational transitions was not obtained in these experiments, cross-section measurements for transitions between specified initial and final rotational states of $Li^+$-$H_2$ lie within the capability of present-day molecular beam technology [8]. The accuracy of existing intermolecular potentials for $Li^+$-$H_2$($D_2$) should permit reliable interpretation of experiments and accurate calculation of rotational transition probabilities.

Rotational excitation of the mixed isotopically substituted hydrogen molecule HD is also of considerable interest. Eccentricity effects [9], i.e., effects arising from the displacement of the center of mass from the center of charge, are expected to be large and to lead to larger rotational cross sections for HD than for $H_2$ and $D_2$. In addition, because the electron distribution in the Born-Oppenheimer approximation is invariant under the operation of inversion for a heteronuclear molecule with equally charged nuclei, the $Li^+$-HD potential can be obtained from the interaction potential for $Li^+$-$H_2$ by a simple translation of coordinates [10] (see next section). The determination of the interaction potential between $Li^+$ and HD is the primary aim of this paper.

Interaction potentials appropriate for rotational excitation and de-excitation are necessary for the evaluation of cross sections which play an integral role in the understanding of a variety of physical phenomena. These include thermal diffusion in polyatomic gases [11], cooling in interstellar space [12], nuclear spin relaxation [13], cooling in nozzle flow [14], and ultrasonic dispersion [15, 16].

The concept of an intermolecular potential implies that the total scattering system can be characterized by a set of electronic quantum numbers that do not change during the course of a collision. From the potential energy surface, the force on each molecule can be determined by evaluating the gradient of the surface.

There is a close relation between the notion of an intermolecular potential and the Born-Oppenheimer approximation. The latter involves the familiar separation of electronic and nuclear motions whereas the former arises from the uncoupling of different electronic motions. In addition, the quantum-mechanical calculation of interaction potentials requires solution of the Schrödinger equation for electronic motion in the Born-Oppenheimer approximation. Therefore, one is confronted with the same difficulties that are encountered in the computation of electronic energies of polyatomic molecules. However, accuracy is more critical here because the interaction energy between two systems is defined as the *difference* between the energy of the composite system and the sum of the energies of the separate species at infinite separation, and is usually the difference between two large numbers. Furthermore, for collision problems, calculations are required for a much larger range of the relative positions and orientations of the molecules.

Until recently, the *ab initio* calculation of interaction energies of even simple systems was so difficult and relatively disappointing in outcome that much effort was spent in calculating semiempirical potential energy surfaces of questionable validity. With the advent of large high-speed digital computers, a resurgence of activity is occurring in this field [17].

The interaction energy can be described by a sum of two terms, the Hartree-Fock (H-F) and the correlation energy contributions [18]. The H-F portion is determined using the best possible self-consistent-field (SCF) wave functions for the composite system and for the infinitely separated collision pair. The remainder required to give the exact nonrelativistic interaction energy is the correlation energy contribution. If an accurate SCF wave function for the total system reduces to the correct product wave function in the nonoverlap region, the interaction energy in the SCF limit, i.e., the H-F interaction energy, is a meaningful approximation to the true interaction energy.

Cases in which the H-F approximation may be expected to be adequate are the interactions between a) two closed-shell systems and b) a closed-shell system and a fragment with one electron outside of a closed shell. For the interaction of weakly polarizable closed-shell ion-molecule systems at large separations, the H-F approximation would again be expected to yield reliable energies because of the smallness of the dispersion interaction for such systems compared to the contributions of classical origin (electrostatic and induction terms) obtainable in the H-F approximation. (The dispersion force is presumed to arise from correlation effects [19].)

In a calculation of the He-$H_2$ interaction potential, Krauss and Mies [20] showed that the interaction energy could be obtained closer to the H-F limit than could the total energy of the system. Recent calculations of potential energy surfaces appropriate for rotational excitation of HF by Li [21] and rotational-vibrational excitation of $H_2$ by $Li^+$ [4] support this finding. For both systems, interaction energies computed at large center of mass separations in the nonoverlap region are an order of magnitude smaller than the nearness of the total energies of the fragments, and therefore of the composite system, to the H-F limit and are in good agreement with perturbation theory results. Previous calculations have demonstrated the adequacy of calculations to H-F accuracy for construction of intermolecular potentials at small separations. On this basis we assumed [4] that the recently computed $Li^+$-$H_2$ surface is very close to the true one.

Because an accurate analytical expression has been determined for the $Li^+$-$H_2$ energy surface [4], a straightforward procedure for constructing a similar expression for $Li^+$-HD is to apply the coordinate transformation mentioned above to the $Li^+$-$H_2$ potential function [22]. However, such a procedure leads to an expression containing exponential functions of an argument (the ion to molecule center of mass separation) that upon transformation becomes an explicit function of angle. Such a functional dependence is inconvenient because the intermolecular potential is no longer separable, a property commonly assumed in formulations of rotational and vibrational excitation by collision [23]. For this reason, alternative methods are investigated in the present paper.

In the next section two methods for obtaining interaction energies for $Li^+$-HD from those for $Li^+$-$H_2$ are described. The resultant interaction energies, least-squares fits, and perturbation theory comparisons are presented and discussed in the succeeding section. Related calculations of potential surfaces for rotational and vibrational energy transfer have recently been surveyed and discussed [24] and need not be described again.

## Determination of interaction energies

• *Method A*

In this method $Li^+$-HD interaction energies are calculated from the previously determined analytical expression for the interaction potential between $Li^+$ and $H_2$ [4(a)] (see Appendix A). Coordinates in the $Li^+$-HD frame at which the interaction energy is desired are transformed to the $Li^+$-$H_2$ system as described below and then the interaction energy is evaluated from the $Li^+$-$H_2$ potential function.

The coordinate system for $Li^+$-HD is displayed in Fig. 1. Here $r_e$ is the equilibrium separation of HD($H_2$), chosen to be 1.4 a.u., $r'$ is the $Li^+$ to center of charge distance, $\theta'$ is the angle formed by $r_e$ and $r'$, $r$ is the $Li^+$ to HD

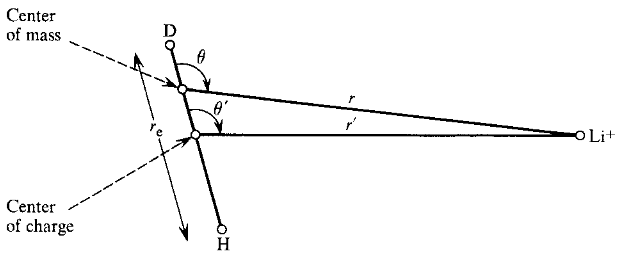


**Figure 1** Coordinates for the $Li^+$-HD system.

center of mass separation, and $\theta$ is the angle formed by $r_e$ and $r$. Note that the HD center of mass is $\frac{1}{3}r_e$ from the D end and that for $H_2$ the center of mass and center of charge are coincident at $\frac{1}{2}r_e$.

From Fig. 1 it is apparent that the transformation of coordinate origin from the center of mass of $H_2$ to the center of mass of HD is simply a translation of $\frac{1}{6}r_e$ from the center of charge in the D direction. If the three-particle system is chosen to lie in the $x$-$y$ plane with the figure axis of the diatomic molecule as the $x$ axis, the coordinates $r$ and $\theta$ are readily obtainable from the relations

$$x = r' \cos \theta' - \tfrac{1}{6}r_e \tag{1}$$

and

$$y = r' \sin \theta', \tag{2}$$

so that

$$\theta = \tan^{-1} (y/x) \tag{3}$$

and

$$r = (x^2 + y^2)^{\frac{1}{2}}. \tag{4}$$

From these equations and the least-squares fit to the $Li^+$-$H_2$ intermolecular potential [4], $Li^+$-HD interaction energies are easily obtained to the accuracy of the analytical representation of the $Li^+$-$H_2$ potential function. These energies are then fit by a nonlinear least-squares procedure to a convenient functional form.

• *Method B*

The fitting of interaction energies to functional forms generally leads to some loss of accuracy. By method A, $Li^+$-HD interaction energies needed for collision problems are the result of two least-squares fits, one in the original $Li^+$-$H_2$ potential function determination and a second for $Li^+$-HD using interaction energies deduced from the $Li^+$-$H_2$ function. Thus it seemed worthwhile to investigate a procedure in which the number of fitting procedures is reduced. This was the motivation for method B in which *ab initio* $Li^+$-$H_2$ interaction energies are used directly to yield $Li^+$-HD interaction energies convenient for generating an analytical representation of the ion-heteronuclear molecule surface.

In the $Li^+$-$H_2$ investigation, the calculation of the least-squares fit to the potential surface was facilitated by the computation of interaction energies at the same value of $r'$ for each value of $\theta'$. Such a selection of points permits a satisfactory fit to be obtained either by fitting the radial dependence first and then the angular dependence, or vice versa. However, the coordinates arising from Eqs. (1) through (4) are not convenient for either starting point. Therefore the following steps were taken to obtain a more satisfactory set of interaction energies for the fitting process.

The procedure consists of interpolation of the $Li^+$-HD total energies [25] at approximately the same value of $r$, i.e., interpolation of those energies arising from a given value of $r'$, in order to determine the energies at selected values of $\theta$ (0, 15°, 30°, $\cdots$ , 180°); this step is followed by inverse interpolation to obtain the value of $r$ corresponding to the chosen value of $\theta$. Implicit in this procedure is the assumption that the dependence of the potential surface on $r'$ and $\theta'$ is separable so that interpolation with respect to these variables separately is a good approximation. For nonreactive interactions such as the present one, it is expected that this sequence of operations will, in general, provide greater accuracy than would the reverse order because of the smaller energy gradient in the $\theta$ direction. Both the $\theta$ and $r$ interpolations were performed utilizing Aitken's iterated method [26] for which the effective convergence, and therefore a measure of the reliability of the one-dimensional interpolation, can be estimated.

With energy points obtained following the operations described above, a least-squares fit to the $Li^+$-HD surface was obtained first for the radial dependence as a tabulation of parameters arising from terms of the trial analytical form for each $\theta$. The set of parameters determined for a given term was then fit to expansions in Legendre polynomials of various lengths for determination of the optimal angular fit. (This procedure was followed for both methods A and B.)

## Results and discussion

Interaction energies generated by the two methods were fit to the expression

$$V(r, \theta) = \sum_{l=0}^{4} v_l(r) P_l(\cos \theta), \tag{5}$$

where, as stated above, $r$ is the $Li^+$ to center of mass separation and $\theta$ is the angle formed by $r$ and the axis of the molecule.

Expressed in electron volts, the $r$-dependent coefficients in Eq. (5) were found by method A to be

$$v_0(r) = 288.30344 \exp(-2.096r) + 414.40595 \times \exp(-1.981r) - 0.268471r^{-2} + 10.66067r^{-3} - 133.6937r^{-4}, \quad (6)$$

$$v_1(r) = 221.83472 \exp(-2.096r) - 530.02542 \times \exp(-1.981r) + 1.7241r^{-2} - 27.24589r^{-3} + 115.1659r^{-4}, \quad (7)$$

$$v_2(r) = 86.26234 \exp(-2.096r) + 191.3853 \times \exp(-1.981r) - 0.736248r^{-2} + 22.8098r^{-3} - 58.80515r^{-4}, \quad (8)$$

$$v_3(r) = -131.1401 \exp(-2.096r) + 11.7189 \times \exp(-1.981r) + 0.26637r^{-2} - 4.0599r^{-3} + 8.7414r^{-4}, \quad (9)$$

$$v_4(r) = 178.2045 \exp(-2.096r) - 104.7287 \times \exp(-1.981r) - 0.0119r^{-2} - 0.3742r^{-3} + 4.5799r^{-4}, \quad (10)$$

and by method B the coefficients are

$$v_0(r) = 564.1172 \exp(-2.11r) + 203.4502 \times \exp(-1.89r) - 0.641379r^{-2} + 15.677776r^{-3} - 150.7479r^{-4}, \quad (11)$$

$$v_1(r) = -63.3565 \exp(-2.11r) - 248.1263 \times \exp(-1.89r) + 1.303575r^{-2} - 22.18757r^{-3} + 101.5846r^{-4}, \quad (12)$$

$$v_2(r) = 208.6548 \exp(-2.11r) - 8.2868 \times \exp(1.89r) + 0.595117r^{-2} + 3.38872r^{-3} + 10.15053r^{-4}, \quad (13)$$

$$v_3(r) = -87.1509 \exp(-2.11r) + 30.2779 \times \exp(-1.89r) - 0.36142r^{-2} + 5.2193r^{-3} - 24.2449r^{-4}, \quad (14)$$

$$v_4(r) = 19.5907 \exp(-2.11r) + 52.0315 \times \exp(-1.89r) - 4.29061r^{-2} + 6.6562r^{-3} - 23.8261r^{-4}. \quad (15)$$

Both sets of expressions are valid for 2 a.u. $\leq r \leq$ 12 a.u.

Equation (5) is a convenient form for representing the intermolecular potential because it permits immediate comparison with various anisotropic potentials used in recent scattering calculations concerned with rotational energy transfer. Furthermore, in such problems, this form gives rise to well-known coupling matrix elements.

As a check on the reliability of the two procedures for generating the $Li^+$-HD surface, SCF calculations were performed for selected geometric configurations. Table 1 contains the results of these computations. Also given are interaction energies $V_A$ and $V_B$, determined from Eqs. (5) through (10) and Eqs. (5) and (11) through (15), respectively, and the difference between the SCF results and $V_i$ ($i$ = A, B). The latter entries, indicated by $\Delta V_A$ and $\Delta V_B$, gauge the extent that the two sets of equations properly describe the surface.

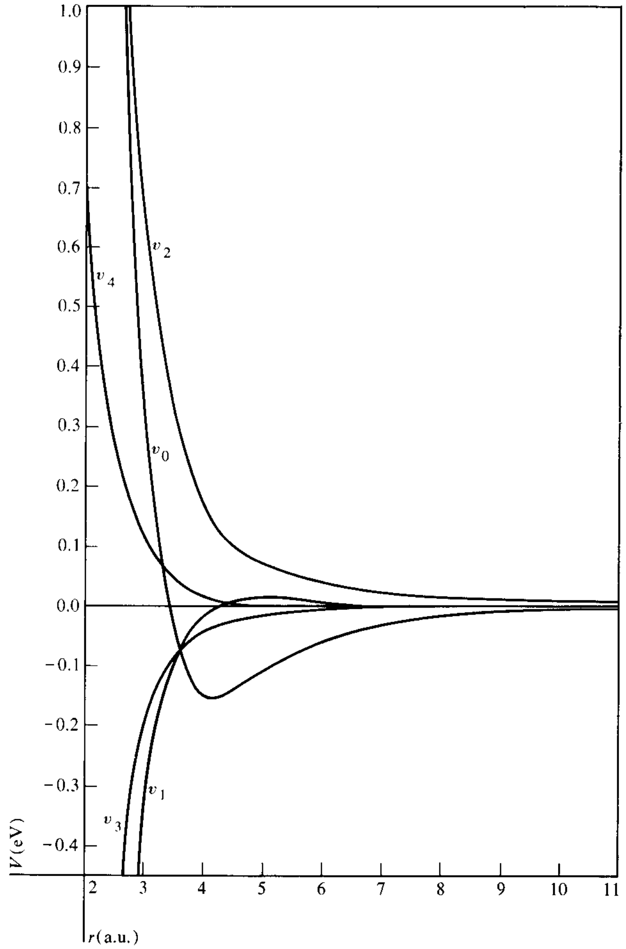


**Figure 2** Radial coefficients of the interaction energy expression for $Li^+$-HD; see Eq. (5).

Since interaction energies determined by method B would be expected to be most in error in regions of the surface with large gradients, i.e., for small values of $r$ in the present case, the decision was made to reduce this effect as much as possible by replacing the interpolated interaction energies in this region with the SCF values for use in the fitting procedure. Comparison of $\Delta V_A$ and $\Delta V_B$ in Table 1 indicates no significant improvement of the function determined by method B over the one obtained by method A.

The radial functions $v_0$ through $v_4$ are illustrated in Fig. 2. Only one set of curves is presented; the two sets of equations for methods A and B yield results that are essentially indistinguishable on the scale plotted. This result is supported by Table 2, which presents a tabulation of the radial functions determined by the two methods. A comparison of even-ordered functions with the analytical representation for $Li^+$-$H_2$ indicates that almost all of the

**Table 1** Comparison of SCF[a] and least-squares interaction energies.

| $\theta$ (deg) | $r$ (a.u.)[b] | $V_{SCF}$[c] | $V_A$ | $\Delta V_A$[d] | $V_B$ | $\Delta V_B$ |
|---|---|---|---|---|---|---|
| 0 | 2 | 5.651 | 5.865 | −0.214 | 5.872 | −0.221 |
| | 3 | 0.537 | 0.535 | 0.002 | 0.546 | −0.009 |
| | 7 | −0.0002 | −0.0013 | 0.0011 | −0.0009 | 0.0007 |
| | 10 | 0.0040 | 0.0051 | −0.0011 | 0.0047 | −0.0007 |
| 15 | 2 | 5.458 | 5.583 | −0.125 | 5.632 | −0.174 |
| 30 | 2 | 4.949 | 4.926 | 0.023 | 5.049 | −0.100 |
| 45 | 2 | 4.306 | 4.274 | 0.032 | 4.414 | −0.108 |
| | 3 | 0.264 | 0.248 | 0.016 | 0.230 | 0.034 |
| | 7 | −0.0188 | −0.0201 | 0.0013 | −0.0203 | 0.0015 |
| | 10 | −0.0031 | −0.0018 | −0.0013 | −0.0024 | −0.0007 |
| 60 | 2 | 3.736 | 3.858 | −0.122 | 3.925 | −0.189 |
| | 3 | 0.133 | 0.134 | −0.001 | 0.129 | 0.004 |
| 75 | 2 | 3.407 | 3.635 | −0.228 | 3.618 | −0.211 |
| | 3 | 0.0409 | 0.0533 | −0.0124 | 0.0751 | −0.0342 |
| 90 | 2 | 3.451 | 3.535 | −0.084 | 3.537 | −0.086 |
| | 3 | 0.0201 | 0.0246 | −0.0045 | 0.0696 | −0.0495 |
| | 4 | −0.237 | −0.236 | −0.001 | −0.236 | −0.001 |
| | 7 | −0.0421 | −0.0430 | 0.0009 | −0.0424 | −0.0003 |
| | 10 | −0.0112 | −0.0102 | −0.0010 | −0.0110 | −0.0002 |
| 105 | 2 | 4.006 | 3.792 | 0.214 | 3.947 | 0.059 |
| | 3 | 0.102 | 0.091 | 0.011 | 0.142 | −0.039 |
| 120 | 2 | 5.265 | 4.919 | 0.346 | 5.268 | −0.003 |
| | 3 | 0.317 | 0.310 | 0.007 | 0.348 | −0.031 |
| 135 | 2 | 7.440 | 7.236 | 0.204 | 7.676 | −0.236 |
| | 3 | 0.675 | 0.698 | −0.023 | 0.714 | −0.039 |
| | 7 | −0.0260 | −0.0258 | −0.0002 | −0.0264 | −0.0004 |
| | 10 | −0.0042 | −0.0042 | 0.0000 | −0.0041 | −0.0001 |
| 150 | 2 | 10.535 | 10.343 | 0.192 | 10.715 | −0.180 |
| 165 | 2 | 13.796 | 13.087 | 0.709 | 13.316 | 0.480 |
| 180 | 2 | 15.322 | 14.188 | 1.134 | 14.344 | 0.978 |
| | 3 | 1.725 | 1.735 | −0.010 | 1.723 | 0.002 |
| | 7 | −0.0037 | −0.0023 | −0.0014 | −0.0040 | 0.0003 |
| | 10 | 0.0041 | 0.0032 | 0.0009 | 0.0043 | −0.0002 |

[a] Obtained using the basis set of Ref. 4(a).
[b] 1 a.u. (length) = 0.52917 × $10^{-8}$ cm.
[c] All energies are in electron volts (eV); 1 a.u. (energy) = 27.210 eV.
[d] $\Delta V_i = V_{SCF} - V_i$ ($i$ = A, B).

additional anisotropy originating from the change of coordinate origin is concentrated in the odd components. It is further observed that both $v_1$ and $v_3$ contribute significantly at short range, but are considerably less important at larger separations.

Table 3 contains a comparison of the interaction energies determined by methods A and B with perturbation theory estimates of the classical (electrostatic plus induction, $E + I$) interaction energies. The perturbation theory results were obtained from the expressions and values of molecular properties given in Appendix B. For $r \geq 5$ a.u., the results of methods A and B and the values of $E + I$ are in reasonable agreement at all angles. The positive interaction energies, which begin at approximately 7 a.u. (0°) and 8 a.u. (180°), are due to the dominance of the quadrupolar term of the electrostatic portion of the interaction energy over the induction contribution in this region (see Appendix B).

From the comparison of the results of methods A and B, there appears to be no readily identifiable reason for

**Table 2** Comparison of $Li^+$-HD potential-function coefficients; $r_e(HD) = 1.4$ a.u.

| $r$ (a.u.) | $v_0$ (eV) A | $v_0$ (eV) B | $v_0$ (eV) $Li^+$-$H_2$ | $v_1$ (eV) A | $v_1$ (eV) B | $v_2$ (eV) A | $v_2$ (eV) B | $v_2$ (eV) $Li^+$-$H_2$ | $v_3$ (eV) A | $v_3$ (eV) B | $v_4$ (eV) A | $v_4$ (eV) B | $v_4$ (eV) $Li^+$-$H_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 5.152 | 5.313 | 5.126 | −2.507 | −2.693 | 3.937 | 4.085 | 3.589 | −1.654 | −1.543 | 0.938 | 0.711 | 0.548 |
| 3 | 0.338 | 0.355 | 0.313 | −0.374 | −0.391 | 0.700 | 0.660 | 0.615 | −0.226 | −0.197 | 0.0977 | 0.119 | 0.0539 |
| 4 | −0.157 | −0.156 | −0.160 | −0.0092 | −0.0113 | 0.170 | 0.171 | 0.163 | −0.0384 | −0.0388 | 0.0141 | 0.0155 | 0.0083 |
| 5 | −0.111 | −0.111 | −0.111 | 0.0150 | 0.0160 | 0.0709 | 0.0720 | 0.0712 | −0.0109 | −0.0114 | 0.0036 | 0.0026 | 0.0024 |
| 6 | −0.0574 | −0.0573 | −0.0575 | 0.0077 | 0.0087 | 0.0414 | 0.0406 | 0.0413 | −0.0050 | −0.0045 | 0.0014 | 0.0012 | 0.0009 |
| 7 | −0.0296 | −0.0296 | −0.0297 | 0.0033 | 0.0038 | 0.0272 | 0.0263 | 0.0269 | −0.0028 | −0.0022 | 0.0005 | 0.0008 | 0.0004 |
| 8 | −0.0159 | −0.0161 | −0.0160 | 0.0018 | 0.0018 | 0.0187 | 0.0184 | 0.0187 | −0.0016 | −0.0014 | 0.0002 | 0.0005 | 0.0001 |
| 9 | −0.0091 | −0.0094 | −0.0090 | 0.0015 | 0.0011 | 0.0132 | 0.0135 | 0.0135 | −0.0009 | −0.0010 | 0.0000 | 0.0002 | 0.0000 |
| 10 | −0.0054 | −0.0058 | −0.0053 | 0.0015 | 0.0010 | 0.0096 | 0.0104 | 0.0100 | −0.0005 | −0.0008 | 0.0000 | 0.0000 | 0.0000 |
| 11 | −0.0033 | −0.0038 | −0.0031 | 0.0016 | 0.0010 | 0.0070 | 0.0082 | 0.0077 | −0.0003 | −0.0007 | 0.0000 | −0.0002 | 0.0000 |
| 12 | −0.0021 | −0.0027 | −0.0019 | 0.0018 | 0.0011 | 0.0053 | 0.0066 | 0.0060 | −0.0001 | −0.0007 | 0.0000 | −0.0003 | 0.0000 |

**Table 3** Comparison of perturbation theory and computed interaction energies.

| $\theta$ (deg) | $r$ (a.u.) | $E + I$[a] (eV) | $V_A$ (eV) | $r$ (a.u.) | $E + I$ (eV) | $V_B$ (eV) |
|---|---|---|---|---|---|---|
| 0 | 4 | −0.146 | −0.0225 | 3.766667 | −0.200 | 0.0124 |
| | 5 | −0.0404 | −0.0321 | 4.766667 | −0.0544 | −0.0382 |
| | 6 | −0.0102 | −0.0113 | 5.766667 | −0.0144 | −0.0142 |
| | 7 | −0.0005 | −0.0007 | 6.766667 | −0.0019 | −0.0017 |
| | 8 | 0.0026 | 0.0034 | 7.766667 | 0.0022 | 0.0028 |
| | 9 | 0.0034 | 0.0046 | 8.766667 | 0.0034 | 0.0040 |
| | 10 | 0.0034 | 0.0047 | 9.766667 | 0.0035 | 0.0040 |
| | 12 | 0.0028 | 0.0039 | 11.766667 | 0.0029 | 0.0033 |
| 45 | 4 | −0.244 | −0.119 | 3.8315 | −0.292 | −0.112 |
| | 5 | −0.0954 | −0.0818 | 4.83261 | −0.110 | −0.0912 |
| | 6 | −0.0438 | −0.0406 | 5.83300 | −0.0495 | −0.0447 |
| | 7 | −0.0225 | −0.0196 | 6.83320 | −0.0250 | −0.0212 |
| | 8 | −0.0125 | −0.0096 | 7.83336 | −0.0138 | −0.0106 |
| | 9 | −0.0074 | −0.0047 | 8.3360 | −0.0081 | −0.0058 |
| | 10 | −0.0046 | −0.0022 | 9.83374 | −0.0050 | −0.0034 |
| | 12 | −0.0020 | −0.0002 | 11.83395 | −0.0021 | −0.0013 |
| 90 | 4 | −0.341 | −0.237 | 4.00273 | −0.340 | −0.237 |
| | 5 | −0.150 | −0.145 | 5.00391 | −0.149 | −0.146 |
| | 6 | −0.0770 | −0.0775 | 6.00366 | −0.0769 | −0.0772 |
| | 7 | −0.0442 | −0.0429 | 7.00144 | −0.0442 | −0.0422 |
| | 8 | −0.0274 | −0.0252 | 7.998098 | −0.0275 | −0.0249 |
| | 9 | −0.0181 | −0.0157 | 9.00130 | −0.0181 | −0.0162 |
| | 10 | −0.0125 | −0.0103 | 10.00128 | −0.0125 | −0.0112 |
| | 12 | −0.0066 | −0.0049 | 12.00113 | −0.0066 | −0.0060 |
| 135 | 4 | −0.241 | −0.120 | 4.1613 | −0.204 | −0.133 |
| | 5 | −0.0931 | −0.107 | 5.1623 | −0.0811 | −0.0981 |
| | 6 | −0.0422 | −0.0554 | 6.1628 | −0.0376 | −0.0480 |
| | 7 | −0.0213 | −0.0270 | 7.1631 | −0.0192 | −0.0231 |
| | 8 | −0.0116 | −0.0134 | 8.16335 | −0.0106 | −0.0119 |
| | 9 | −0.0067 | −0.0067 | 9.1635 | −0.0062 | −0.0065 |
| | 10 | −0.0040 | −0.0033 | 10.16382 | −0.0037 | −0.0039 |
| | 12 | −0.0016 | −0.0006 | 12.16402 | −0.0015 | −0.0015 |
| 180 | 4 | −0.141 | 0.0799 | 4.233333 | −0.103 | 0.0124 |
| | 5 | −0.0371 | −0.0400 | 5.233333 | −0.0269 | −0.0382 |
| | 6 | −0.0079 | −0.0199 | 6.233333 | −0.0048 | −0.0142 |
| | 7 | 0.0012 | −0.0045 | 7.233333 | 0.0021 | −0.0017 |
| | 8 | 0.0039 | 0.0020 | 8.233333 | 0.0041 | 0.0028 |
| | 9 | 0.0044 | 0.0042 | 9.233333 | 0.0044 | 0.0040 |
| | 10 | 0.0042 | 0.0047 | 10.233333 | 0.0042 | 0.0040 |
| | 12 | 0.0033 | 0.0041 | 12.233333 | 0.0032 | 0.0033 |

[a] See Appendix B for the definitions of the perturbation theory expressions; $E$ denotes electrostatic energy and $I$, induction energy.

choosing one procedure over the other. However, the procedures *per se* suggest rather clearly defined choices. If analytical expressions are available for a related potential energy surface, the computational effort involved in method A is considerably less than that of method B and leads to essentially identical results. In the event that an analytical representation is not available nor readily obtainable, method B presents a practicable method for generating the interaction potential for an isotopically related system.

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## Appendix A

The potential function for the interaction between $Li^+$ and $H_2$ at a separation of 1.4 a.u. was determined in Ref. 4(a) to be

$$V(r', \theta') = v_0(r') + v_2(r')P_2(\cos\theta') + v_4(r')P_4(\cos\theta') \tag{A1}$$

for 2 a.u. $\leq r' \leq$ 12 a.u., where (in eV)

$$v_0(r') = 599.3367 \exp(-2.03r') + 84.9030 \times \exp(-2.06r') + 6.6183r'^{-3} - 118.6957r'^{-4}, \tag{A2}$$

$$v_2(r') = -153.946 \exp(-2.03r') + 366.0221 \times \exp(-2.06r') + 11.9284r'^{-3} - 19.0837r'^{-4}, \tag{A3}$$

$$v_4(r') = -365.08443 \exp(-2.03r') + 408.99089 \times \exp(-2.06r') - 0.4614379r'^{-3} + 4.15251r'^{-4}. \tag{A4}$$

See Fig. 1 for the definitions of $r'$ and $\theta'$.

## Appendix B

Interaction energies valid at long range for the nonoverlap region have been computed for comparison with results of the present calculations. In the usual manner, the perturbation theory result for the classical contribution was written as

$$V(r, \theta) = v(r, \theta)_{\mathrm{electrostatic}} + v(r, \theta)_{\mathrm{induction}}. \tag{B1}$$

The expressions used were

$$v(r, \theta)_{\mathrm{electrostatic}} = q_{\mathrm{Li}^+}[\mu_{\mathrm{HD}} r^{-2} P_1(\cos\theta) + \Theta_{\mathrm{HD}} r^{-3} P_2(\cos\theta)] \tag{B2}$$

and

$$v(r, \theta)_{\mathrm{induction}} = -q^2_{\mathrm{Li}^+} r^{-4}[\tfrac{1}{2}\alpha_{\mathrm{HD}} + \tfrac{1}{3}(\alpha_\parallel - \alpha_\perp)_{\mathrm{HD}} P_2(\cos\theta)]. \tag{B3}$$

The numerical values used were

$\mu_{\mathrm{HD}} = 1.47 \times 10^{-3}$ a.u. [27(a)],

$\Theta_{\mathrm{HD}} = 0.460$ a.u. [27(b)],

$\alpha_\parallel = 6.38049$ a.u. [27(c)],

$\alpha_\perp = 4.57769$ a.u. [27(c)],

$\alpha_{\mathrm{HD}} = 2.7792$ a.u. [27(d)].

Results for $\theta = 0, 45°, 90°, 135°$ and $180°$ are presented in Table 3.

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