Hartree–Fock and Gordon–Kim interaction potentials for scattering of closed-shell molecules by atoms: (H_2CO,He) and (H_2,Li^+)

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The Gordon–Kim (GK) electron gas model for calculating the forces between closed-shell atoms and molecules is applied to the He–H_2CO and Li^+–H_2 systems. GK interaction energies are computed following the original theory and also including the self-energy correction suggested by Rae. GK interaction energies, neglecting correlation, are found to be in qualitative accord with Hartree–Fock (HF) interaction energies for the two systems. However, quantitative discrepancies are noted which are possible sources of error if GK potential energy surfaces are used to compute accurate scattering cross sections.

I. INTRODUCTION

Intermolecular forces determine both the dynamics of molecular collisions and the equilibrium properties of matter. Because of their fundamental role in both dynamic and static phenomena, a variety of experimental methods have been used to obtain information about them.[1] Despite an abundance of data, however, relatively little *detailed* information has been obtained this way. One reason for this deficiency is the difficulty of reliably determining the dependence of the interaction potential on (1) the internal coordinates of the separate molecules involved in the collision and on (2) the relative orientation of the scattered pair during the course of the encounter. Unfortunately, measurements of equilibrium properties sample only a small range of coordinate values near the minimum whereas measurements of collision phenomena generally suffer from the opposite problem of reflecting an average of large regions of the energy surface.[1a]

It is usually possible experimentally to obtain the intermolecular distance dependence of a potential energy hypersurface.[2] For atom–atom interactions, of course, the interatomic distance is the only coordinate. For more complex systems, however, it is common practice to analyze molecular data in terms of a *spherical* interaction potential which represents an average over internal molecular coordinates. This is usually done by the nonunique procedure of assuming a model potential form and adjusting the parameters of the potential to reproduce the scattering data.

Because of the importance of interaction potentials and the difficulties associated with their experimental determination, considerable effort has been directed toward obtaining potentials *a priori* by solving the electronic Schroedinger equation. Although such a procedure can, in principle, yield solutions of arbitrary accuracy, in practice severe approximations usually must be made for all but the simplest systems. Fortunately, the errors introduced by these approximations are now well documented.[3] Methods are currently available to accurately describe the regions of potential energy surfaces required for rotational and vibrational energy transfer by collisions occurring on a single electronic potential energy surface. These include the Hartree–Fock (HF) and configuration interaction (CI) methods which have been particularly well studied[3] and for which efficient computer programs are available. Because the cost of these approaches increases rapidly with the number of electrons in the system, their use for the calculation of interaction potentials for collision studies has been severely limited.[3–5] For this reason, numerous efforts have been made to find less time-consuming yet accurate approximations.

Gordon and Kim (GK)[6] have recently proposed a method for generating interaction potentials between closed-shell systems. Despite its simplicity, this method appears to be quite reliable based on comparisons with experimental data. Extensive comparisons have been severely limited, however, by lack of experimental and theoretical information, especially knowledge of the dependence of the interaction potential on internal molecular coordinates, so that most previous tests of this method have been limited to closed-shell atom–atom[6] and atomic ion–atom interactions.[7] Because the GK method is both simple and economical (being orders of magnitude faster than the HF approximation provided one of the interaction partners is spherically symmetric), it is increasingly being applied to compute potential energy surfaces needed for the study of rotational and vibrational energy transfer in molecular collisions. For this reason, it is desirable to delimit the capability of the method as precisely as possible, particularly for describing the dependence of intermolecular potentials on internal molecular coordinates.

In this paper, we compare the GK electron gas model with more accurate *ab initio* procedures for atom–molecule interactions. The next section presents a brief review of the theoretical background including a summary of the GK formalism and modifications required for the treatment of molecule–molecule interactions. The latter have not been presented previously. In Sec. III, HF and GK results for the interaction potential between He and H_2CO and between Li^+ and H_2 are compared and discussed. Section IV summarizes the findings of this study.

II. THEORY

The interaction potential between two systems, A and B, is defined as the total energy of the combined A–B system minus the energy of A and B at infinite separation and at rest. Invoking the usual Born–Oppenheimer ("clamped nuclei") approximation permits separation of the electronic and nuclear motions. The electronic energy as a function of the nuclear coordinates defines a potential energy surface. In the present study, we restrict consideration to single electronic potential surfaces.

Gordon and Kim[6] write the energy as a sum of Coulombic, kinetic, exchange, and correlation terms

$$E = E_C + E_K + E_X + E_{\text{corr}} . \tag{1}$$

As usual, the first three terms comprise the HF energy. The interaction potential V may be written

$$V = E_{AB} - E_A - E_B \tag{2}$$

$$= V_C + V_K + V_X + V_{\text{corr}} \tag{3}$$

$$= V_{HF} + V_{\text{corr}} . \tag{4}$$

Each of the terms in Eq. (3) is computed from the electronic charge density. GK further assume that the total charge density ρ_{AB} of the A–B system is simply the superposition of the separate HF charge densities ρ_A and ρ_B, i.e.,

$$\rho_{AB} = \rho_A + \rho_B . \tag{5}$$

The terms V_K, V_X, and V_{corr} are evaluated from uniform electron gas expressions which depend only on the local charge density.[6] These terms have the form

$$V_i = \int d\mathbf{r}[\rho_{AB}E_i(\rho_{AB}) - \rho_A E_i(\rho_A) - \rho_B E_i(\rho_B)] , \tag{6}$$

where $i \equiv K$, X, and corr. Here, following GK, E_K, E_X, and E_{corr} are evaluated by a simple free electron gas approximation. For molecule–molecule interactions, Eq. (6) is evaluated by three dimensional (3D) numerical quadrature; for atom–atom interactions one integration can be done analytically owing to symmetry so that only a 2D numerical quadrature is required.

The Coulomb term is computed from exact electrostatic relations and consists of four terms which describe nuclear-nuclear and electron–electron repulsion, and nuclear–electron attraction. They may be written

$$V_C = V_{\alpha\beta} + V_{12} + V_{1\beta} + V_{2\alpha} , \tag{7a}$$

where

$$V_{\alpha\beta} = \sum_{\alpha \subset A}\sum_{\beta \subset B} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} , \tag{7b}$$

$$V_{12} = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho_A(\mathbf{r}_1)\rho_B(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} , \tag{7c}$$

$$V_{1\beta} = \sum_{\beta \subset B} Z_\beta \int d\mathbf{r}_1 \frac{\rho_A(\mathbf{r}_1)}{|\mathbf{R}_\beta - \mathbf{r}_1|} , \tag{7d}$$

$$V_{2\alpha} = \sum_{\alpha \subset A} Z_\alpha \int d\mathbf{r}_2 \frac{\rho_B(\mathbf{r}_2)}{|\mathbf{R}_\alpha - \mathbf{r}_2|} . \tag{7e}$$

Note that $R_\alpha(R_\beta)$ are the positions and $Z_\alpha(Z_\beta)$ are the charges of the nuclei in molecule A(B). Equation (7b) is trivially computed from the geometry of the scattered molecules. Equations (7d) and (7e) can be computed by 3D numerical integration; in practice, the apparent singularities at the nuclei do not pose a problem. Equation (7c) presents some difficulty since it requires, in general, a 6D integration. Note that these same integrals [Eqs. (7c)–(7e)] are required for a HF calculation of ρ_A and ρ_B. For wavefunctions expanded in the familiar Slater and Gaussian basis functions,[3] methods for evaluating these terms are well known.[8] If computed by these methods, however, the integrals would have to be evaluated for many combinations of basis functions and re-evaluated for each of the geometries at which the interaction energy is desired. Such a procedure would negate the main advantage of the GK method, its inherent speed relative to HF and CI.

It is possible to reduce Eq. (7c) to a 3D integral, at least formally, by rewriting it in terms of the electrostatic potential of one of the charge distributions (see, for example, Ref. 9). Thus,

$$V_{12} = \int d\mathbf{r}_1 \rho_A(\mathbf{r}_1) P_B(\mathbf{r}_1) , \tag{8}$$

where P_B, the electrostatic potential due to ρ_B, is given by

$$P_B(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{\rho_B(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} . \tag{9}$$

No net computational savings will result, of course, unless P_B can be obtained more simply than the 3D integration implied in Eq. (9). Such will be the case, for example, when B is spherically symmetric (i.e., an atom) so that P_B can be obtained by a 1D integration. (If the atomic wavefunction is expanded in Slater or Gaussian basis functions, P_B can also be obtained analytically. Furthermore, P_B can be obtained analytically for any polyatomic wavefunction expanded in Gaussian basis functions.) The greatest saving in computing time for spherical B, however, comes not so much from the ease of calculating the electrostatic potential but from the possibility of tabulating it once at a suitable radial grid and then obtaining values as necessary by interpolation. Kim[9] has demonstrated the possibility of 2D tabulation and interpolation for homonuclear diatomic molecules as well, but for the general case in which neither molecule has high symmetry, the GK method is likely to lose its computational advantage over the HF approach.

The functional relations used by GK for the kinetic,

TABLE I. Interaction energies (°K) for He–H_2CO.[a]

R	θ	φ	HF	GKHF	GKCO	GKRHF	GKRCO
3.5	0	0	59839.6	46261.8	44477.6	61772.9	59988.7
3.5	180	0	92169.2	57317.2	54753.1	78733.4	76169.3
4.0	0	0	21571.6	16491.0	15487.1	23523.4	22519.9
4.0	180	0	40460.6	26048.4	24332.4	38054.6	36340.0
4.5	0	0	7498.5	5256.2	4742.1	8256.4	7742.3
4.5	180	0	16500.1	11054.5	10011.5	17453.8	16410.8
5.0	0	0	2508.8	1464.5	1206.7	2679.6	2421.3
5.0	45	0	1332.1	501.0	344.2	1127.4	970.6
5.0	45	90	1063.3	425.8	277.6	1000.9	852.7
5.0	90	0	592.5	321.0	147.0	948.8	774.8
5.0	90	90	540.9	79.9	−26.2	413.0	306.9
5.0	135	0	14510.0	11370.3	10473.8	17141.8	16245.3
5.0	135	90	1593.1	1073.7	763.7	2376.2	2066.2
5.0	180	0	6356.0	4253.6	3628.6	7496.0	6871.1
6.0	0	0	229.0	47.4	−9.8	222.6	165.5
6.0	180	0	777.9	370.4	172.3	1088.8	890.8
7.0	0	0	−11.1	−7.9	−18.0	14.2	4.1
7.0	45	0	−37.8	−6.0	−11.4	4.7	−0.3
7.0	45	90	−22.7	−6.0	−11.1	4.1	−0.9
7.0	90	0	−5.2	−13.6	−24.6	8.2	−2.8
7.0	90	90	−4.8	−7.6	−12.3	1.6	−3.2
7.0	135	0	314.8	55.3	−29.1	315.5	231.5
7.0	135	90	7.9	−23.1	−45.8	26.2	3.5
7.0	180	0	55.1	−22.4	−75.2	111.5	58.7

[a] $1\,°K = 3.1668 \times 10^{-6}$ a.u.

exchange, and correlation energies are derived from a statistical treatment of an infinite uniform electron gas.[6] Because of their statistical basis, the applicability of these equations to the fairly small number of electrons contained in molecular systems has been questioned. In particular, Rae[10] argues that GK incorrectly include the self-exchange energy. Because the exchange term and the electron–electron Coulomb term are intimately related and because GK compute these terms from different models, the validity of Rae's argument is not entirely clear. Rather, in the modelistic spirit of the GK method it would seem appropriate to choose the exchange energy to best reproduce experimental (or more accurate *ab initio*) results. In this regard, Cohen and Pack[11] suggest a procedure that retains Rae's exchange correction, but replaces the statistical correlation energy at large internuclear separations by the van der Waals energy.

III. APPLICATIONS, RESULTS, AND DISCUSSION

A. Rigid asymmetric top: (H_2CO,He)

The interaction potential between He and H_2CO is of considerable interest because of the anomalous absorption of H_2CO in the interstellar medium.[12] The absorption is anomalous because it implies an effective temperature for the lowest levels of formaldehyde which is below both the temperature of the isotropic radiation and the expected kinetic temperature. Townes and Cheung[12b] suggest that the apparent non-Boltzmann distribution in H_2CO may be due to collisions with He or H_2. To test this supposition requires an accurate interaction potential and the calculation of the dynamical motion of the system on the energy surface. For convenience, He is selected as the scatterer in the present study, although H_2 is within existing computational capability. The additional coordinates that would have to be sampled for a proper study involving H_2, however, imply considerable additional computation deemed best deferred at this time.

Interaction energies for He–H_2CO are given in Table I for selected geometries at which HF computations were carried out. The coordinates employed are R, the intermolecular distance between He and the center of mass of H_2CO, and θ, the orientation angle which prescribes the direction of incidence of He to the c.m. of H_2CO. Here $\theta = 0°$ corresponds to approach from the O atom end along the CO bond. The azimuthal angle φ is measured from the plane of H_2CO, i.e., $\varphi = 0°$ is the plane of H_2CO. By symmetry, the angular ranges are $0° \le \theta \le 180°$ and $0° \le \varphi \le 90°$. All results presented are for the H_2CO geometry used by Goodfriend *et al.*[13] and more recently by Winter *et al.*[14] of $r(CO) = 1.21$ Å, $r(CH) = 1.12$ Å, and $\theta(HCH) = 118°$, which is quite close to a more recent determination[15] of $r(CO) = 1.208$ Å, $r(CH) = 1.116$ Å, and $\theta(HCH) = 116°31'$.

In Table I, GKHF designates GK results neglecting the free-electron gas correlation contribution and GKCO identifies GK values including this contribution. Similarly, GKRHF specifies interaction energies resulting from Rae's self-energy correction to the GK procedure neglecting the correlation term and GKRCO is the corresponding result including the correlation contribution.

The HF calculations were obtained using the IBMOL-6 computer code[16] and a basis set that has been given previously for H_2CO[17] and for He.[18] The same H_2CO basis set and a comparable Slater basis set for He were used to generate the HF charge densities required in the various GK procedures. All GK results were determined using a version of the computer program POTLSURF[19] modified to include d functions.

Figures 1–5 present plots of interaction energies obtained following the various procedures discussed above. The θ dependence of the interaction in the plane of $H_2CO(\varphi = 0°)$ is shown in Fig. 1 for $R = 5$ a.u. One sees initially a small repulsion due to O, for He incident

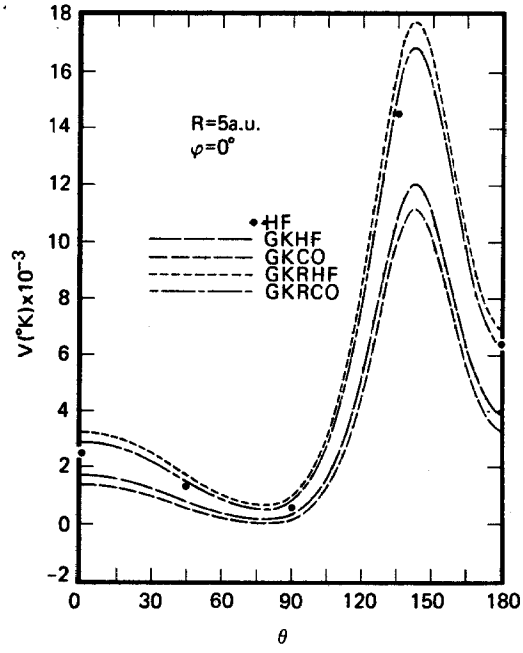

FIG. 1. Angular dependence of the interaction energy for He incident in the plane of H_2CO at a c.m. separation of 5 a.u.

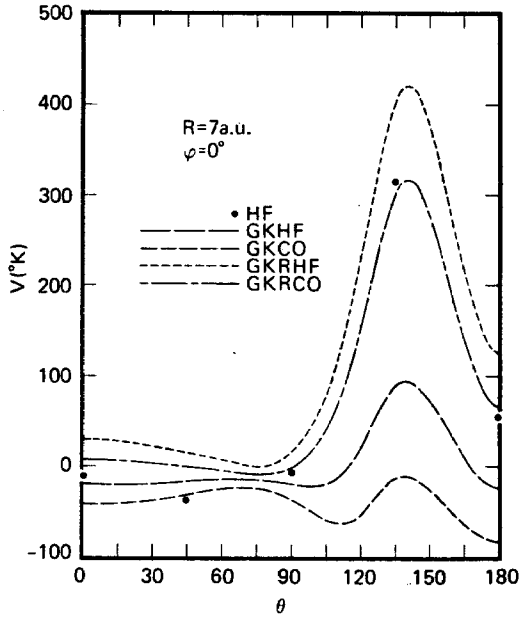

FIG. 2. Angular dependence of the interaction energy for He incident in the plane of H_2CO at a c.m. separation of 7 a.u.

along the CO bond ($\theta = 0°$), which decreases to a minimum for approaches nearly perpendicular to the CO bond ($\theta \simeq 80°$). As θ is further increased, the repulsion mounts, at first partly due to C but predominantly due to H, and reaches a maximum for $\theta \simeq 140°$. Figure 2 is a similar plot for $R = 7$ a.u. Note in this figure, in contrast to Fig. 1, that the GK variants do not in each case qualitatively follow the behavior of the HF results, particularly for $\theta \lesssim 75°$. This is most likely due to the inability of the GK procedures to describe the smaller interaction as the intermolecular distance approaches the region of the minimum for various orientations. In both Figs. 1 and 2, GKRHF and GKRCO results are generally closer to HF values than GKHF and GKCO values. Because the standard of comparison in the present study is the HF approximation, emphasis is placed on the comparison of HF with GKHF and GKRHF.

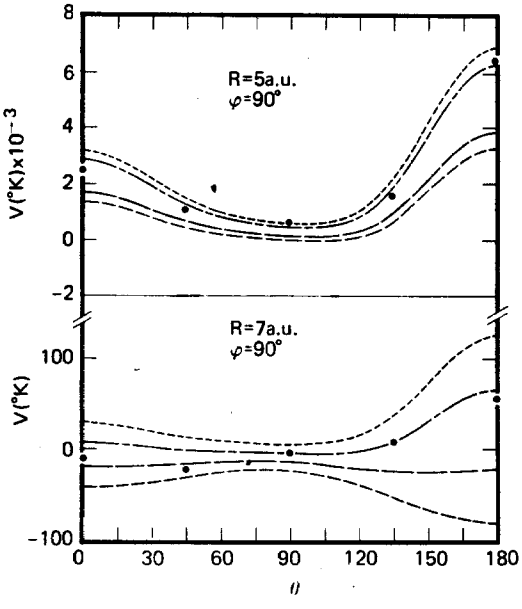

FIG. 3. Angular dependence of the interaction energy for He incident in the perpendicular bisector plane of H_2CO at c.m. separations of 5 and 7 a.u.

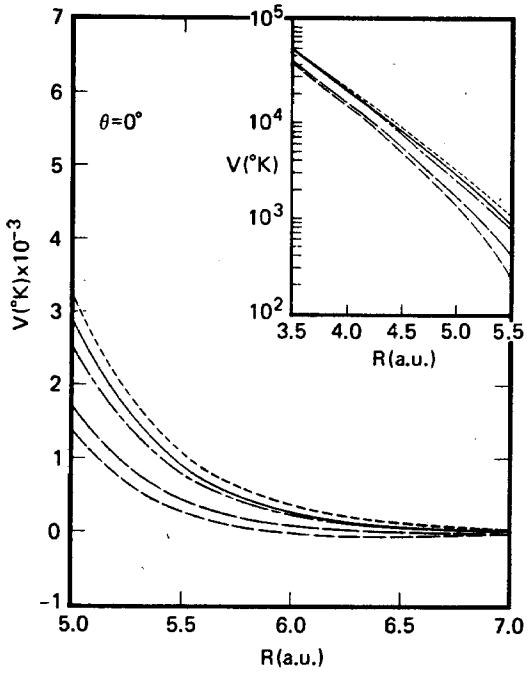

FIG. 4. Interaction energy for He incident collinearly with the CO bond of formaldehyde from the O-atom end.

Figure 3 presents plots of the θ dependence of the interaction potential in each approximation for He incident in the bisector plane normal to the H_2CO plane, the $\varphi = 90°$ direction, for the R values displayed in Figs. 1 and 2. For $R = 5$ a.u. the GKRHF curve is clearly in closer agreement with the HF result than the

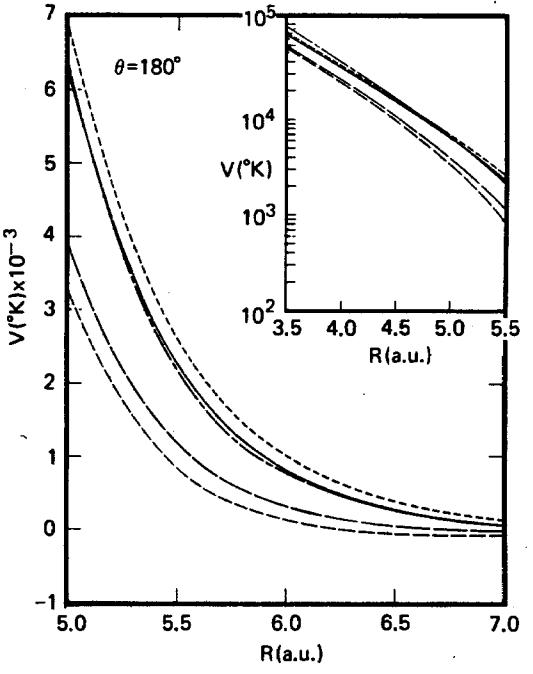

FIG. 5. Interaction energy for He incident collinearly with the CO bond of formaldehyde from the C-atom end.

TABLE II. Interaction energies (eV) for Li^+-H_2.[a]

		$\theta=0°$			$\theta=90°$	
R \ r	1.0	1.4	2.0	1.0	1.4	2.0
	6.030	9.309	17.257	3.345	3.512	3.372
	4.756	7.554	14.899	2.209	2.190	1.909
2.0	5.773	8.836	16.662	3.009	3.033	2.749
	3.405	5.554	10.058	1.796	1.981	2.025
	2.780	4.536	8.794	1.189	1.203	1.065
2.25	3.444	5.389	10.051	1.713	1.774	1.661
	1.875	3.226	6.103	0.856	0.969	1.013
	1.655	2.775	5.440	0.614	0.623	0.543
2.50	2.085	3.355	6.318	0.954	1.006	0.960
	0.987	1.815	3.609	0.323	0.363	0.361
	1.008	1.745	3.472	0.297	0.292	0.229
2.75	1.283	2.129	4.077	0.516	0.546	0.519
	0.498	0.986	2.190	0.036	0.024	−0.020
	0.631	1.127	2.276	0.125	0.107	0.049
3.0	0.806	1.379	2.690	0.266	0.276	0.249
	0.211	0.502	1.148	−0.100	−0.146	−0.226
	0.409	0.751	1.533	0.036	0.009	−0.049
3.25	0.520	0.916	1.813	0.126	0.120	0.086

[a]Order of entries in the table: HF, GKHF, and GKRHF. Energies in electron volts (eV): 1 eV = 3.6752×10^{-2} a.u. Distances in atomic units (a.u.): 1 a.u. = 0.52917×10^{-8} cm.

GKHF curve. For $R=7$ a.u., however, the agreement between GKRHF and HF is less satisfactory but the GKRHF plot does have more of the general features of the HF result than the GKHF curve, which is qualitatively different.

In Fig. 4, the interaction energy is plotted versus R for C_{2v} geometry of the $He-H_2CO$ system for O-atom end collisions. Again, the GKRHF result is in closer accord with the HF one than the GKHF curve. This finding is maintained for He approaching from the opposite direction (C-atom end) for C_{2v} geometry as shown in Fig. 5.

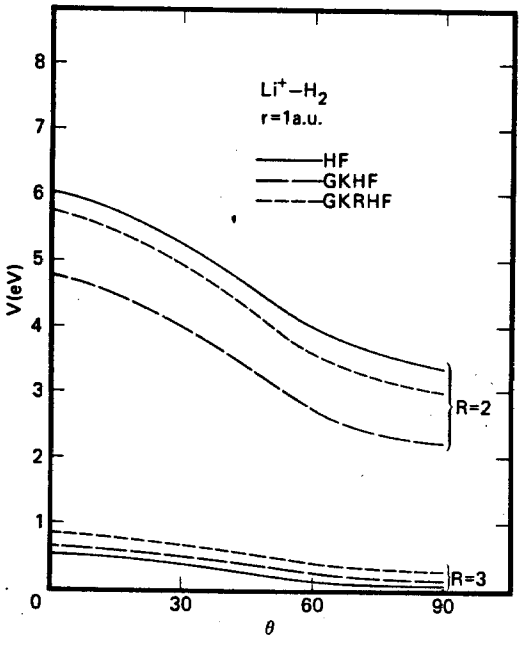

FIG. 6. Anisotropy of the interaction between Li^+ and H_2 for a H–H distance of 1 a.u. and selected c.m. distances.

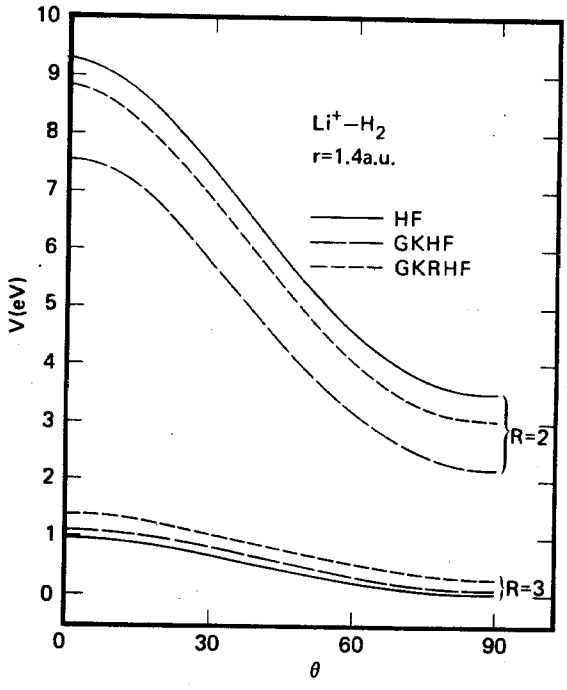

FIG. 7. Anisotropy of the interaction between Li^+ and H_2 for a H–H distance of 1.4 a.u. and selected c.m. distances.

B. Vibrating rotator: Li^+-H_2

Recent molecular beam measurements[20,21] of vibrational and rotational excitation of H_2 by Li^+ impact have led to the calculation of accurate HF[22,23] and CI[23] interaction potentials required for computation of collision dynamics. These potential energy surfaces have been shown to be quite similar[24] and to lead to essentially the same integral and differential cross sections in accurate quantum-mechanical computations of rotational energy transfer cross sections.[25]

Because the GK formulation does not properly describe polarization effects,[26] comparisons for this system are restricted to a limited range of $R(\sim 2-3$ a.u.) lying inside the region of the potential minimum ($R_{min} \simeq 4-5$ a.u.) for arbitrary orientations θ. Here R is the distance between Li^+ and the c.m. of H_2, θ is the angle formed by the H_2 figure axis and the direction of incidence of Li^+ to the c.m. of H_2, and r is the internuclear separation of H_2.

Because the HF and CI potentials are indistinguishable on a scale useful for comparison with GK results, we restrict consideration to interaction energies computed using the HF, GKHF, and GKRHF methods only. The basis set and other details associated with the HF calculations have been given previously.[22] Slater HF basis sets are used to construct the charge densities required for the GK method. Table II presents a compilation of interaction energies used to construct the figures that follow.

The anisotropy of the potential energy surface ob-

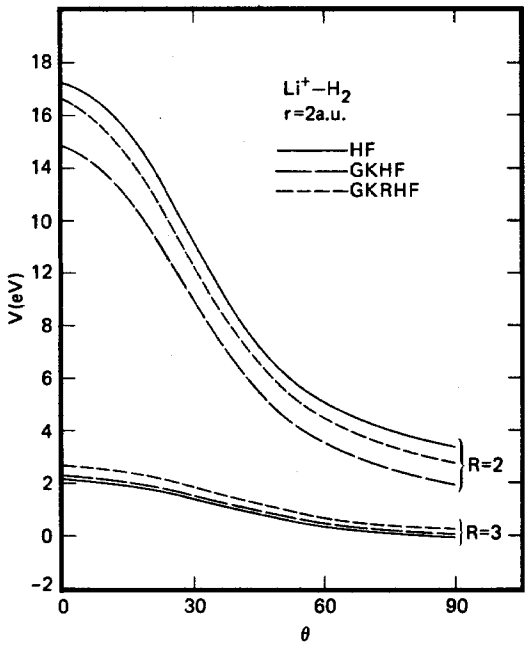

FIG. 8. Anisotropy of the interaction between Li^+ and H_2 for a H–H distance of 2 a.u. and selected c.m. distances.

tained using each of the methods is presented for $R=2$ and 3 a.u. in Fig. 6 for $r=1$ a.u., in Fig. 7 for $r=1.4$ a.u., and in Fig. 8 for $r=2$ a.u. Close examination of these figures does not provide a basis for preferring either the GKHF or GKRHF methods. At each r, both methods display the same qualitative curvature although often differing from HF by as much as 0.5 eV.

The R dependence for the collinear ($\theta=0°$) and perpendicular ($\theta=90°$) approaches is seen in Fig. 9 for $r=1$ a.u., in Fig. 10 for $r=1.4$ a.u., and in Fig. 11 for $r=2$ a.u. In these figures, one sees that use of

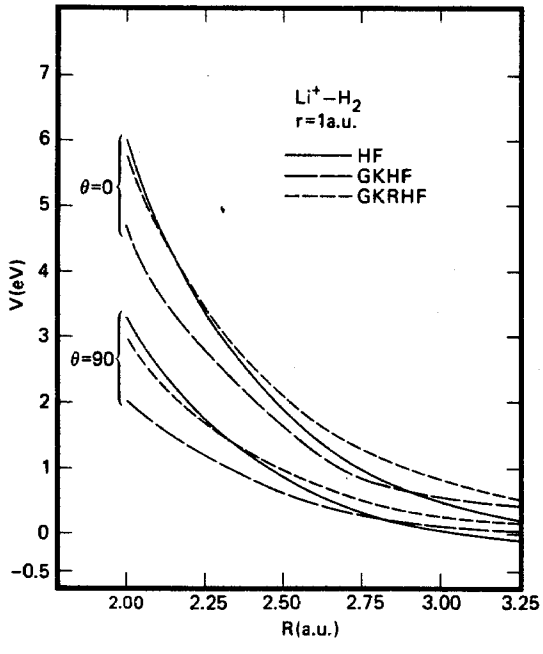

FIG. 9. Interaction energy for collinear ($\theta=0°$) and perpendicular ($\theta=90°$) approaches of Li^+ to H_2 for H–H distance of 1 a.u.

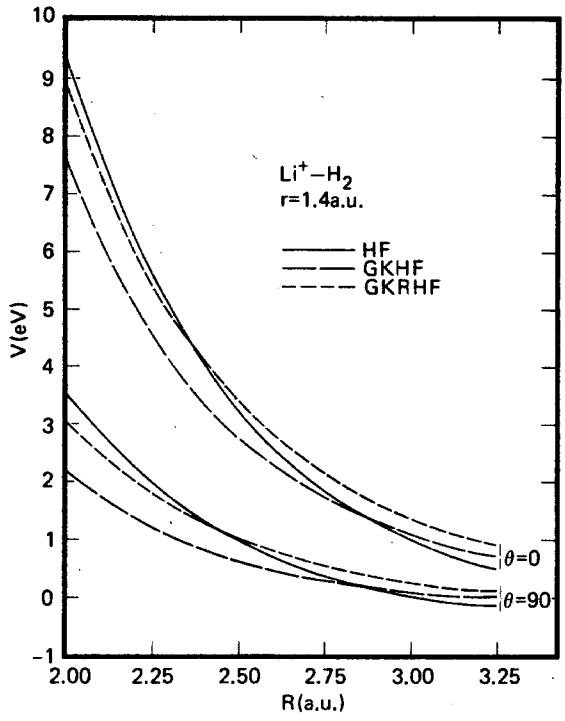

FIG. 10. Interaction energy for collinear ($\theta=0°$) and perpendicular ($\theta=90°$) approaches of Li^+ to H_2 for H–H distance of 1.4 a.u.

the GKHF and GKRHF procedures leads to a similar pattern of differences at each of the three r values plotted. For directions of incidence of Li^+ shown ($\theta=0°$ and 90°), the GKRHF energy lies closer to the HF result at smaller R whereas the GKHF result is closer to the HF one at the larger R values.

The adequacy of the GK procedures for describing

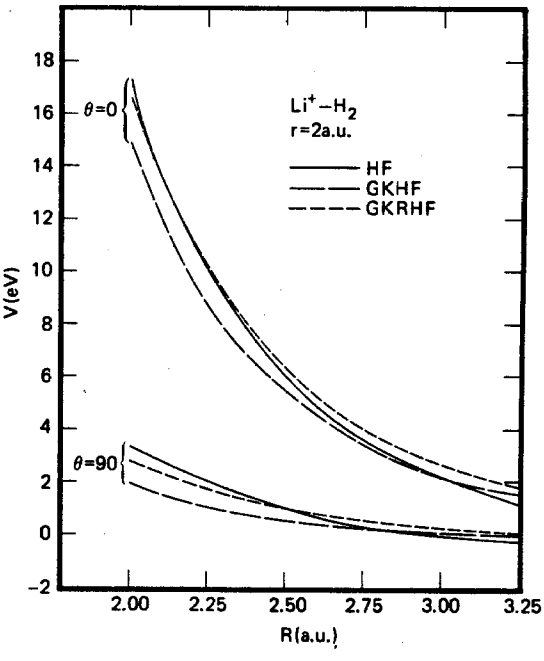

FIG. 11. Interaction energy for collinear ($\theta=0°$) and perpendicular ($\theta=90°$) approaches of Li^+ to H_2 for H–H distance of 2 a.u.

the vibrational coordinate dependence of the Li^+-H_2 interaction is shown for collinear and perpendicular approaches of Li^+ to H_2 at $R=2$ a.u. in Fig. 12 and at $R=3$ a.u. in Fig. 13. Again, the GK procedures are seen to yield results in qualitative accord with the HF results, but with energy differences that, based on previous studies,[27] would imply rather different scattering behavior.

IV. SUMMARY AND COMMENTS

The GK electron gas model has been extended to interactions of closed-shell molecules with atoms. To provide a basis for estimating its accuracy, the method has been applied to the interaction of H_2CO (treated as a rigid rotor) with He for comparison with new Hartree–Fock results for the system. Similar electron gas calculations have been performed for Li^+ interacting with H_2 treated as a vibrating rotor for comparison with published HF values.[22]

For short-range repulsive interactions in the two systems, the GK model is found to provide at least a qualitatively correct description of the dependence of the potential on intermolecular separation, orientation angles, and (for Li^+-H_2) vibrational coordinate. This is gratifying considering the simplicity of the model. It should be recalled that there is currently little data available—either experimental or theoretical—concerning the dependence of intermolecular forces on internal coordinates. Although this information can be obtained in principle from rigorous *ab initio* calculations, such studies can become prohibitively expensive for mapping multidimensional potential surfaces. Therefore cheaper and more approximate methods such as the GK model should be very useful for studying collisional energy transfer.

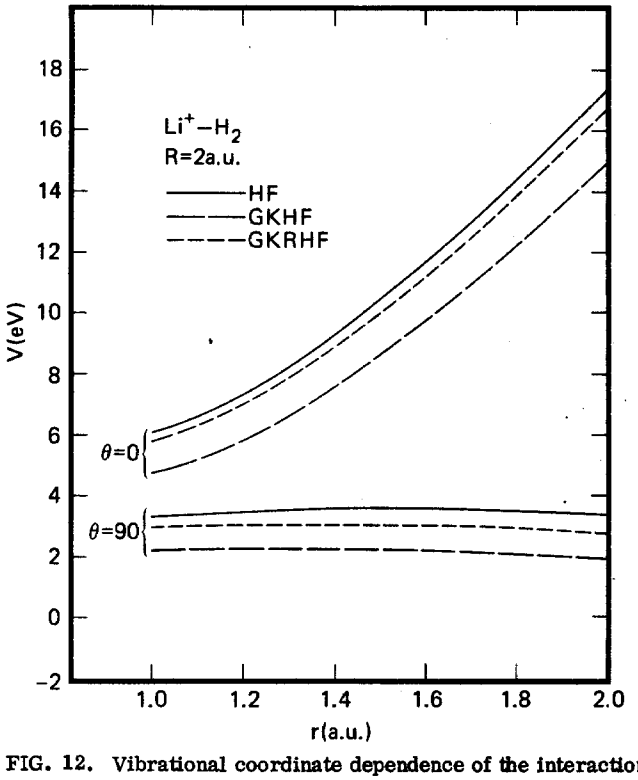

FIG. 12. Vibrational coordinate dependence of the interaction energy for collinear ($\theta=0°$) and perpendicular ($\theta=90°$) approaches of Li^+ to H_2 at $R=2$ a.u.

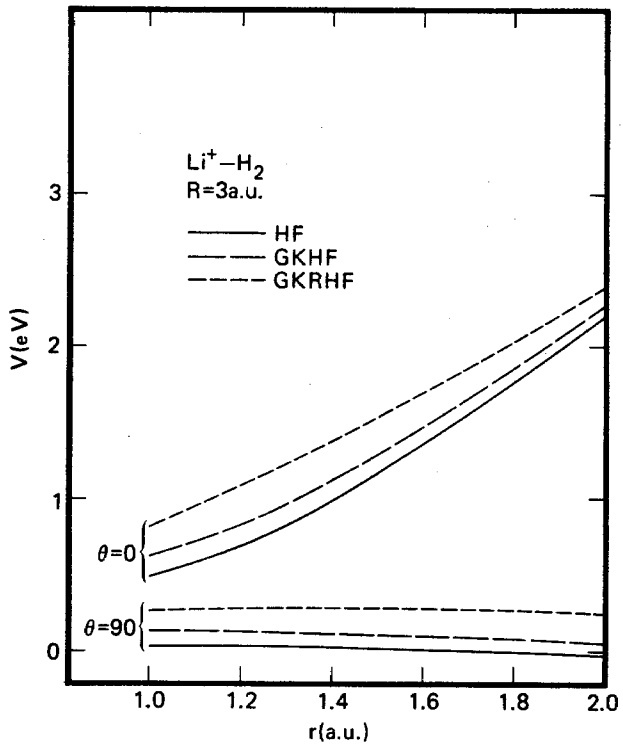

FIG. 13. Vibrational coordinate dependence of the interaction energy for collinear ($\theta=0°$) and perpendicular ($\theta=90°$) approaches of Li^+ to H_2 at $R=3$ a.u.

Modifications to the GK model have received some attention in the literature, especially the self-energy correction first suggested by Rae.[10] We have explicitly considered Rae's correction. For H_2CO–He its use improves agreement with HF results, but for Li^+-H_2 it is difficult to choose between the original and modified methods. It appears to be generally (but not always) true that the original GK method gives smaller repulsive interaction energies than the HF method while Rae's correction gives larger values. A more important observation, perhaps, is that the differences between these modifications are comparable to errors in the model itself, such as those due to nonuniformity of the charge distribution and the exclusion of polarization effects.

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