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ON THE ISOTROPIC AND LEADING ANISOTROPIC TERMS OF THE H–H_2 POTENTIAL ENERGY SURFACE

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SCF and SCF CI calculations were performed to obtain the isotropic V_0 and leading anisotropic V_2 terms of the H–H_2 potential surface An analytic estimate of V_0 is obtained by adding to the near Hartree–Fock curve a function which approximately fits the correlation energy at small R and reduces at large R to the multipolar expansion of the dispersion energy The behavior of V_2 is also discussed

1 Introduction

A fundamental example of chemical reactions with activation barriers is the D + H_2 system, D + H_2 ⇌ DH + H. It also provides an important prototype for studying inelastic processes in chemical reactive systems because the relatively high-energy barrier to reaction means that under many low-energy conditions exchange is negligible [1].

Several ab initio calculations of the H_3 potential energy surface have been reported [2], the most extensive and accurate (within less than 1 kcal mol^{-1}) being that of Siegbahn and Liu (SL) [3,4]. However, like most previous ab initio calculations studying the exchange process, the SL surface is restricted to the small internuclear separations which encompass the saddle-point geometry; the rate of the exchange process is, to a large extent, determined by the topology of the surface close to this point. Analytical potentials in the (R_1, R_2, R_3) interparticle coordinates which closely fit the SL ab initio data and allow a reliable extrapolation into regions of the H_3 configuration space uncovered by the ab initio results have also been reported [5–7] ‡.

Ab initio valence bond calculations of Norbeck et al. [8,9] using a comparatively modest optimized (2s1p) Slater basis set extend to larger H–H_2 separations (R) but still did not include the van der Waals minimum. Existing information about this region comes primarily from the inversion of transport and cross section measurements. However, transport data depend only weakly on the H–H_2 interaction potential as has been demonstrated by the wide range of potential parameters which have been found to provide an equally good representation of the experimental data [2]. More specific and consistent information is obtained from molecular beam scattering data [10–13]. Yet, there is a discrepancy of ≈45% in the well depths of the most popular molecular beam potentials, and of ≈6% and ≈5%, respectively, in the location of the van der Waals minimum (R_m) and the distance of energy zero (σ) for these potentials.

For quantum scattering calculations it is convenient to express the H–H_2 interaction potential as a Legendre polynomial expansion,

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[‡] In ref [6] the coordinates R and r are labelled X and x respectively.

$$V(R,r_e,\theta) = \sum_l V_l(R,r_e)\, P_l(\cos\theta). \qquad (1)$$

where r_e is one bond distance fixed at the H_2 equilibrium geometry and θ is the angle made by the internuclear axis of this pair with R, the separation of the remaining atom from the centre of mass of the diatomic. The expansion potentials, particularly $l = 0$ and 2, play an important role in inelastic and reactive scattering (see ref. [8] and references therein) and they can be obtained from a complete analytical potential $V(R_1, R_2, R_3)$ by integration or from ab initio data by a least-squares fitting procedure.

At short atom–molecule separations, V_0 has an approximate inverse exponential dependence on R that is reliably given by the SL ab initio results. Conversely, the weakly attractive long-range regions of V_0 are conveniently described by the asymptotic $1/R$ dispersion series expansion,

$$-V_{\mathrm{disp}}(R) = C_6R^{-6} + C_8R^{-8} + C_{10}R^{-10} + \qquad (2)$$

which is normally truncated after the first few terms. Yet this expansion (2) is based on a second-order perturbation treatment which takes no account of overlap and exchange effects and it diverges at small R where these effects are significant. The divergence can be avoided by damping the expansion. An example of this is the universal potential function for closed-shell interactions proposed by Ahlrichs et al. [14],

$$V(R) = V_{\mathrm{HF}}(R) + V_{\mathrm{disp}}(R)D(R), \qquad (3)$$

$$D(R) = \exp[-\beta(1.28\, R_\mathrm{m}R^{-1} - 1)^2], \quad R \leqslant 1.28\, R_\mathrm{m}, \qquad (4)$$

$$D(R) = 1, \quad R > 1.28\, R_\mathrm{m}. \qquad (5)$$

where β is a scaling parameter originally assumed to be unity, R_m is the location of the van der Waals minimum which is self-consistently determined, and V_{HF} is a Hartree–Fock repulsion curve. This functional form has recently been used by Torello and Dondi [13] who fitted H–H_2 differential cross section data by trial and error adjustment of the parameters in a modified Born–Meyer (MBM) potential,

$$V_{\mathrm{HF}}(R) = A \exp[-R(b_0 + b_1R)]. \qquad (6)$$

Another approach to this problem is to use accurate ab initio CI data from small R and extrapolate outwards [5,6]. A third approach, which is also possible in the case of the H–H_2 system, is to interpolate between the accurate ab initio data obtained for small R and the dispersion expansion, valid at large R, by choice of a suitable damping function. For this it is necessary to have an accurate ab initio estimate of V_{HF} at large R. However the only theoretical information at large R comes from early perturbation calculations [15,16]. Although perturbation theory could in principle afford an accurate means to determine the small interaction energies involved, the approximations made in evaluating the molecular integrals and the simplicity of the molecular wavefunctions used cast doubt on the reliability of these calculations.

In an attempt to elucidate the discrepancy between existing H–H_2 interaction potentials, we have performed SCF and SCF CI calculations for a range of values going beyond the van der Waals minimum and obtained estimates of V_0 and V_2 over this range. We also tested the validity of truncating eq. (1) at small R by performing SCF calculations at several values of θ.

2. SCF calculations

SCF calculations were performed for a H atom approaching a H_2 molecule with fixed bond length (r_e = 1.4 a_0 ‡) as a function of R and θ. We considered values of R between 1.6 a_0 and 9.0 a_0 with $\theta = 0°$ ($C_{\infty v}$ symmetry) and 90° (C_{2v} symmetry). A few SCF calculations were also performed for θ = 30.5556°, 54.7356° and 70.1243° (all C_s symmetry) to allow the importance, at small R, of the $l > 2$ terms in the Legendre expansion (1) to be investigated and, as a result, a more reliable estimate of V_0 and V_2 in this region. All calculations employed the (4s3p1d) gaussian basis set recommended by Siegbahn and Liu [4]. Although the Siegbahn–Liu basis set may not contain sufficiently diffuse functions to describe the long-range dispersion forces in a CI calculation, we believe that it is sufficient to obtain a potential of near Hartree–Fock quality. The results obtained are given in table 1, and from these we have estimated the harmonic components of the H–H_2 interaction potential given in table 2. Basis-set superposition

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‡ 1 bohr (a_0) = 1 au of bond length = 5.29177 × 10^{-11} m, 1 hartree (E_h) = 1 au of energy = 4.3598 aJ

Table 1
Calculated SCF and SCF CI energies of $H(R,\theta) + H_2(r = 1.4\ a_0)$, in atomic units, for the Siegbahn–Liu [4] basis set

R (a_0)	SCF					SCF CI	
	$\theta = 0°$	$\theta = 30.5556°$	$\theta = 54.7356°$	$\theta = 70.1243°$	$\theta = 90°$	$\theta = 0°$	$\theta = 90°$
1.6	−1.436907	−1.495332	−1.528953	−1.529647	−1.525671		
2.0	−1.556533	−1.564464	−1.567019	−1.565620	−1.564402	−1.615087	−1.617779
2.25	−1.579838				−1.581624		
2.5	−1.593117	−1.594159	−1.594882	−1.594992	−1.595002	−1.650016	−1.644034
2.75	−1.602998				−1.605286		
3.0	−1.610832	−1.611538	−1.612454	−1.612871	−1.613079	−1.660317	−1.658213
3.5	−1.621608				−1.623173		
4.0	−1.627596	−1.627841	−1.628209	−1.628396	−1.628492	−1.669729	−1.669818
4.5	−1.630692				−1.631152		
5.0	−1.632208				−1.632430	−1.672648	−1.672667
5.5	−1.632921				−1.633022	−1.673062	−1.673047
6.0	−1.633245				−1.633290	−1.673221	−1.673195
6.5	−1.633388				−1.633407	−1.673270	−1.673247
7.0	−1.633450				−1.633458	−1.673278	−1.673261
8.0	−1.633487				−1.633488	−1.673267	−1.673258
9.0	−1.633493				−1.633493	−1.673255	−1.673251
∞	−1.633494	−1.633494	−1.633494	−1.633494	−1.633494	−1.673241	−1.673241

Table 2
Harmonic components, in kcal mol^{-1}, of the $H{-}H_2$ ($r = 1.4\ a_0$) SCF and SCF CI interaction potentials

R (a_0)	SCF						SCF CI			
	V_0 [a]	V_0 [b]	V_2 [a]	V_2 [b]	V_4 [b]	V_6 [b]	V_0 [a]	V_0 [c]	V_2 [a]	V_2 [c]
1.6	86.23	72.95	37.13	24.95	21.73	3.692		61.60		26.48
2.0	45.00	42.87	3.292	1.209	3.470	0.740	35.36	31.67	1.126	−0.922
2.25	32.92		0.748							
2.5	24.55	24.34	0.788	0.595	0.335	0.0630	17.08	16.32	−2.502	−2.597
2.75	18.18		0.957							
3.0	13.28	13.23	0.940	0.898	0.0811	0.0100	8.990	8.699	−0.880	−0.911
3.5	6.804		0.655					4.477		0.170
4.0	3.326	3.320	0.375	0.370	0.0102	0.0001	2.167	2.100	0.0371	−0.041
4.5	1.566		0.193					0.838		−0.044
5.0	0.714		0.0926				0.364	0.266	0.0079	−0.006
5.5	0.317		0.0424				0.119		−0.0063	
6.0	0.138		0.0187				0.0234		−0.0106	
6.5	0.0587		0.0080				−0.0085		−0.0098	
7.0	0.0246		0.0033				−0.0160		−0.0074	
8.0	0.0041		0.0005				−0.0125		−0.0036	
9.0	0.0006		0.0001				−0.0071		−0.0017	

[a] Values obtained from the energies of table 1 for $\theta = 0°$ and 90° assuming a two-term Legendre expansion (1).

[b] Values obtained from a least-squares fit to the data of table 1 for $\theta = 0°$, 30.56°, 54.74°, 70.12° and 90° using a four-term Legendre expansion (1).

[c] Ref. [5], values obtained from the complete least-squares potential surface by integration

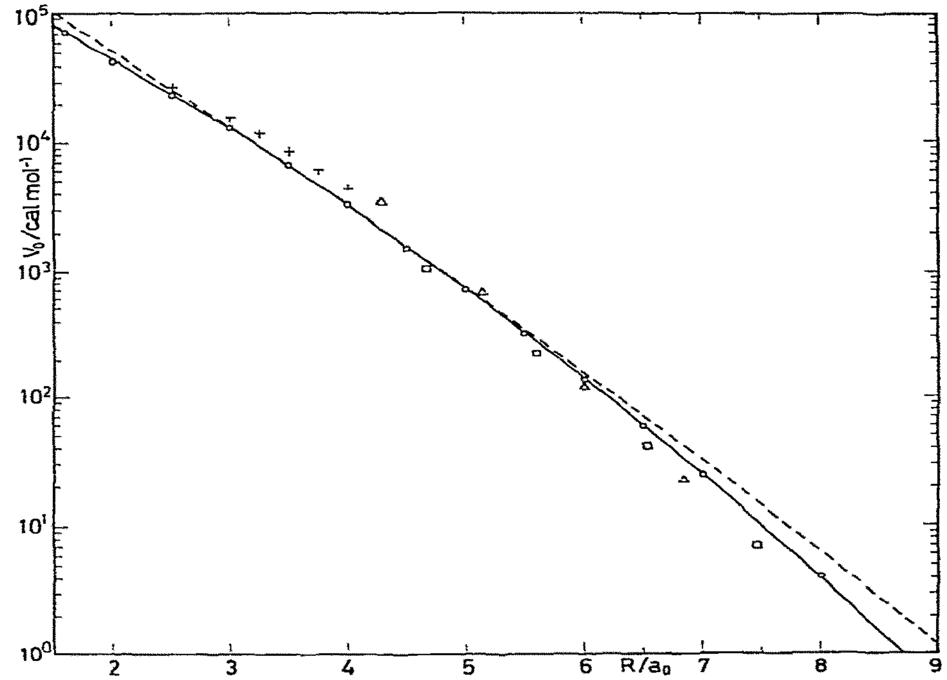

Fig. 1. Spherically averaged H–H$_2$ (r = 1.4 a_0) repulsive potentials. First-order perturbation theory results □ ref. [15], △ ref. [16]. SCF calculations + ref. [9], ○ this work. Modified Born–Meyer analytic potentials – – – ref. [13], —— this work.

errors were negligible: $10^{-6}E_h$ and $7\times10^{-6}E_h$ at R = 6.5 a_0 and R = 2.5 a_0 respectively. Our SCF results for V_0 can be well fitted by a modified Born–Meyer potential (6) with A = 403.48 kcal mol^{-1}, b_0 = 0.97919 a_0^{-1} and b_1 = 0.05775 a_0^{-2}, root-mean-square deviation is 0.44 kcal mol^{-1} and typical errors are ≈3%. They agree surprisingly well with the Torello–Dondi empirical Hartree–Fock curve in the range $3.0 \leqslant R \leqslant 5.0$ a_0, and lie considerably lower in energy than those of Norbeck et al. [8,9] (see fig. 1).

Comparison of the two- and four-term Legendre expansions suggests that the two-term truncation is valid except in the strongly repulsive region of the potential ($R < 2.5$ a_0). Our estimate of the leading anisotropic term V_2 shows a minimum at $R \approx 2.5$ a_0, but still remains positive for all R. Most previous estimates of V_2 have shown a minimum in this region but have found V_2 to be negative there (see fig. 8 of ref. [6]).

3. Interpolating V_0

Having obtained a near Hartree–Fock curve for V_0 we used the universal potential (3)–(5) of Ahlrichs et al. [14] to include correlation effects. However, this approach gives poor agreement with the spherically averaged potentials from the analytical fits to the SL data [5,6] at small R, even when β is treated as an adjustable parameter.

A better approach is to interpolate between the CI data obtained at small R and the dispersion expansion valid at large R by choosing a suitable damping function in (3). A plot of the function $f(R)$,

$$f(R) = \ln\left[1 - \frac{V_{\mathrm{HF}}(R) - V_0^{\mathrm{TH}}}{C_6R^{-6} + C_8R^{-8} + C_{10}R^{-10}}\right]R^{-2}, \quad (7)$$

where V_{HF} and V_0^{TH} are our SCF results and the fitted CI data of Truhlar and Horowitz [5] respectively, against R^2 is nearly linear in the range $1.6 < R < 4.0$ a_0 as shown in the insert in fig. 2. All SCF energies have been taken from column b of table 2 except that for R = 3.5 a_0 which was from column a. Values for C_6, C_8 and C_{10} are those of Meyer[‡]: 8.813, 163.87 and

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[‡] W. Meyer, quoted in ref. [13].

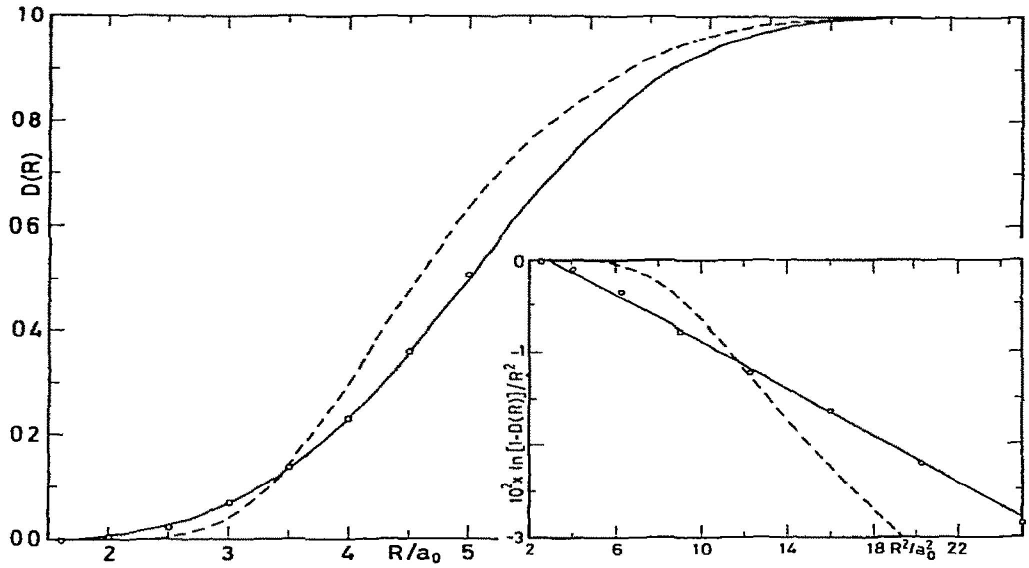

Fig 2 Spherically averaged H–H$_2$ (r = 1 4 a_0) dispersion damping factors $D(R) = (V_{HF} - V)/(C_6R^{-6} + C_8R^{-8} + C_{10}R^{-10})$ – – – ref [13], —— this work, eq (8), ○ calculated values from the SCF energies of the present work and the CI data of ref [5] Shown in the insert is the approximate linear dependence of the calculated points when plotted as $\ln[1 - D(R)]/R^2$ versus R^2

4023 2 au respectively. This suggests that a damping function of the form

$$D(R) = 1 - \exp[-R^2(d_1 + d_2R^2)] \tag{8}$$

might provide a simple means to interpolate for $R >$ 2 a_0 between long- and short-range potentials. This function has the advantage that it is analytic (continuous in all derivatives) for all R and thus it allows short- and long-range potentials to merge smoothly.

The linear constants d_1 and d_2 were determined from a least-squares fit to points in the region $1.6 \leqslant R \leqslant 4\ 0\ a_0$ using the relationship

$$f(R) = \ln[1 - D(R)]/R^2 . \tag{9}$$

All points carried an equal weighting. This fit gave $d_1 = -0\ 0036256a_0^{-2}$ and $d_2 = 0.0012572a_0^{-4}$, and was essentially indistinguishable from one with the point $R = 4.5\ a_0$ included

We cannot expect the damping function (8) to be valid at small R, both because it is negative, although small in absolute value, for $R < 1.7\ a_0$ and because

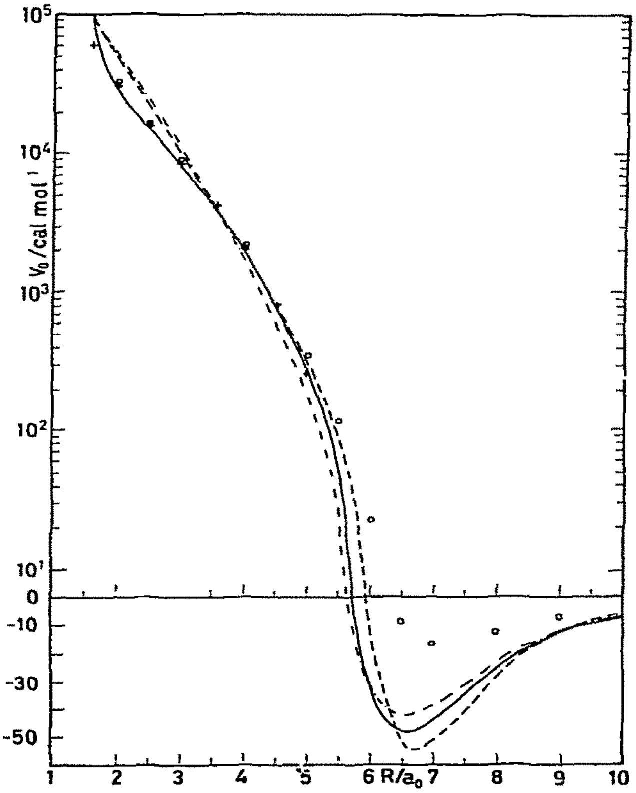

Fig 3 Spherically averaged H–H$_2$ (r = 1 4 a_0) potentials ab initio CI calculations + ref. [5], ○ this work, semi-empirical (empirical) functions – – – ref [10], –·–·– ref. [13], ——— this work, eqs (3), (6) and (8)

Table 3
Comparison between the van der Waals well parameters given by the H–H_2 isotropic potential of this work and those of recent molecular beam potentials, separation of zero-energy σ, separation of minimum-energy R_m and well depth ϵ

Ref	Model	σ (a_0)	R_m (a_0)	ϵ (kcal mol^{-1})
[10]	BMSV [a)]	5.93	6.71	0.054
[11]	LJ(12,6) [b,c)]	5.93	6.65	0.046
[11]	exp(16.8,6) [b,d)]	5.93	6.56	0.060
[12]	exp(12,6) [d)]	5.84	6.65	0.041
[12]	exp(14,6) [d)]	5.63	6.33	0.055
[13]	MBMD [e)]	5.66	6.56	0.042
this work	MBMD [f)]	5.73	6.58	0.049

[a)] Three-region Born–Meyer–spline–van der Waals ($-C_6R^{-6} - C_8R^{-8}$) potential.

[b)] For $R \leqslant \sigma$, $V(R)$ is the potential of ref. [10].

[c)] Lennard-Jones (6–12) potential $V(R) = \epsilon[(R_m/R)^{12} - 2(R_m/R)^6]$.

[d)] Modified Buckingham (6-exp) potential, $V(R) = [\epsilon/(1-6/\alpha)]\{(6/\alpha)\exp[(1-R/R_m)] - (R_m/R)^6\}$.

[e)] Modified Born–Meyer dispersion potential, this work eqs. (3)–(6).

[f)] Modified Born–Meyer dispersion potential, this work eqs. (3), (6) and (8).

there is a discontinuity in the ab initio surface at $R = \frac{1}{2}r_e = 0.7\ a_0$ for collinear geometries. Yet in this region V_0 should be extremely repulsive, rising faster than exponential, and is thus of no great concern for most practical purposes.

Fig. 3 shows the final spherical potential V_0, given in analytic form by eqs. (3), (6) and (8). Our curve deviates by no more than 9% from the Truhlar–Horowitz least-squares surface in the range $1.7 < R < 4.0\ a_0$ where their V_0 is expected to be most accurate. Table 3 compares the parameters of the van der Waals well of the present potential with previous estimates from molecular beam data. Our results suggest a well depth ϵ for V_0 intermediate between that of Gengenbach et al. [10] and Torello and Dondi [13] and are in approximate agreement with the latter authors as far as σ and R_m are concerned.

4. SCF CI calculations

SCF CI calculations were performed in the region $2.0 \leqslant R \leqslant 9.0\ a_0$ for $\theta = 0°$ and $90°$. All single and double excitations from the ground-state SCF configuration which were $^2A_1$ in C_{2v} symmetry were considered, giving 1694 and 1946 configurations for C_{2v} and $C_{\infty v}$ geometries, respectively. No configuration, besides the ground state, had a coefficient greater than 0.05 in any calculation and thus further root functions were not deemed appropriate. However, one cannot expect these calculations to be as accurate as the complete CI of Siegbahn and Liu [3,4] in that we ignore triple excitations. Indeed, this approach gives an energy for the $D_{\infty h}$ geometry ($R_1 = R_2 = \frac{1}{2}R_3 = 1.75\ a_0$) which differs by $4.77 \times 10^{-3}\ E_h$.

Table 1 gives our SCF CI results, and table 2 gives V_0 and V_2 estimated using a two-term Legendre expansion. Fair agreement is found at small R with V_0 and V_2 obtained from the TH [5] surface.

With our limited basis and CI we only obtain, at $R = 6.5\ a_0$, about half the dispersion energy predicted by the empirical multipole expansion (2). We also find that V_2 changes sign at about $R = 5.5\ a_0$ in qualitative agreement with previous semi-empirical estimates [6], but that the van der Waals minimum is deepest at collinear geometries. However we note the relatively large values of V_2 in this region which may be an indication that other values of θ have to be considered in order to obtain V_2 accurately.

5. Conclusions

We have shown that by using near Hartree–Fock results and a damping function of simple form for dispersion (correlation) effects we have interpolated between the areas well described by the multipole expansion and accurate ab initio data. This analytic function gives characteristics of the isotropic potential in agreement with data from molecular beam experiments and lends itself easily to dynamical studies. It has also been shown that the universal damping factor of the potential of Ahlrichs et al. [14] cannot account for the known ab initio data on H–H_2 and is perhaps responsible for the disagreement, at $R > 5.0\ a_0$, between our Hartree–Fock curve and that experimentally determined by Torello and Dondi [13].

Investigation of the leading term in the anisotropic potential at the SCF level suggests that a two-term truncation of the Legendre expansion is valid except at small R, $R < 2\ 5\ a_0$. Thus, one may expect that a reasonably accurate estimate of V_2 can also be obtained from the $\theta = 0°$ and 90° interaction potentials in a way similar to that we used to get V_0. for such an approach to the He–H_2 and Ne–H_2 systems, see ref [17] However. one requires for this accurate estimates of the anisotropies of the C_6. C_8 and C_{10} coefficients

Limited calculations at the SCF CI level suggest that there is still work to be done on the anisotropic potential at large R.

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References

[1] D G Truhlar and R E Wyatt, Ann Rev. Phys Chem 27 (1976) 1
[2] D G Truhlar and R E. Wyatt. Advan Chem Phys 36 (1977) 141
[3] B Liu, J Chem Phys 58 (1973) 1925
[4] P Siegbahn and B Liu, J Chem Phys 68 (1978) 2457
[5] D G Truhlar and C J Horowitz, J Chem Phys 68 (1978) 2466
[6] A J C Varandas J Chem Phys 70 (1979) 3786
[7] A A Wu, Mol Phys 38 (1979) 843
[8] J M Norbeck, P R Certain and K T Tang, J Chem Phys 63 (1975) 590
[9] J M Norbeck and P R Certain, J Chem Phys 63 (1975) 4127
[10] R Gengenbach Ch Hahn and J.P Toennies, J. Chem Phys 62 (1975) 3620
[11] W Welz, Dissertation, University of Bonn (1976)
[12] N Hishinuma, J Phys Soc Japan 41 (1976) 1733.
[13] F Torello and M G Dondi, J Chem. Phys 70 (1979) 1564
[14] R Ahlrichs, R Penco and G Scoles, Chem Phys 19 (1977) 119
[15] H Margenau, Phys Rev 66 (1944) 303
[16] R A Mason and J O Hirschfelder, J Chem Phys 26 (1957) 756
[17] K T Tang and J.P Toennies, J Chem Phys 68 (1978) 5501