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"THE ENERGY OF INTERACTION BETWEEN TWO HYDROGEN ATOMS BY THE GAUSSIAN-TYPE FUNCTIONS"

by

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1. 4th row from bottom of page 2 should be read:

   the energy is given by . . .

2. 1st row of page 3 should be read:

   Atomic integrals[a]

3. 1st rows of page 4 and 5 should be read:

   Continuing Table 1.

4. After the end of Table 1 of page 5, one should add:

   a. $F(x) = \frac{1}{2}\sqrt{\frac{\pi}{x}}\,\mathrm{erf}(\sqrt{x}) = \Phi(\frac{1}{2}, \frac{3}{2}; -x) = e^{-x}\Phi(1, \frac{3}{2}; x)$

   where $\Phi(a,c;x)$ is the confluent hypergeometric function.

THE ENERGY OF INTERACTION BETWEEN TWO HYDROGEN ATOMS BY THE GAUSSIAN-TYPE FUNCTIONS*

by

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ABSTRACT

The interaction of two hydrogen atoms in their ground states is investigated with a Hirschfelder-Linnett type of wave function in which the exponentials are replaced by Gaussian-type functions. It is found that the long-range interaction is not properly described with the functions, although the same functions reasonably approximate the molecular energy near the equilibrium separation. The explicit formulae for the atomic integrals are tabulated.

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1. Introduction

It is a well known fact that the Gaussian-type function[1,2] gives the simple form of integrals, which are necessary in evaluation of atomic or molecular energy in quantum mechanical treatments. Furthermore, many center integrals are easily reduced to one center form without elaborate manipulation. However it is known also that one needs a large basis set in order to attain the accuracy comparable to the results due to Slater-type basis set. Therefore, if one is interested ~~to~~ in the interaction energy of two systems, such as two hydrogen atoms, the Gaussian is still appealing, provided that the error in the molecular energy is constant practically over whole range of the internuclear separation R.

There exists several calculations for the system of the two hydrogen atoms which agree with the experiment for a limited range of the internuclear separation R[3-6]. However, there are very few theoretical treatments which are good both for small and large separations. Especially with small number of basis functions, there is only one work exists, which may fall into this catagory. The work is due to Hirschfelder and Linnett[7].

The objective of this work is to investigate the interaction of two hydrogen atoms with the Gaussian counterpart of the Hirschfelder-Linnett function (neglecting ionic term). The results are not too promising, especially in long range. For small separation, the error in molecular energy is reasonably small considering the extreme simplicity of the trial functions. This very fact, inconstancy of the error with respect to the internuclear separation R, is the greatest

obstacle for the evaluation of potential energy dependence on R.

2. Calculation

For the $^1\Sigma_g^+$ state of the hydrogen molecule, we employ three Gaussian type trial functions,

$$\Psi_0 = (1+P_{12})\, S_A(1)\, S_B(2) \tag{1}$$

$$\Psi_1 = (1+P_{12})\left(S_A(1)\, S_B(2) + \alpha\, P_{zA}(1)\, P_{zB}(2)\right) \tag{2}$$

$$\Psi_2 = (1+P_{12})\left(S_A(1)\, S_B(2) + \beta\, P_{zA}(1)\, P_{zB}(2) + \gamma\left(P_{xA}(1)\, P_{xB}(2) + P_{yA}(1)\, P_{yB}(2)\right)\right) \tag{3}$$

where

$$S_A(1) = e^{-\zeta r_{A1}^2} \tag{4}$$

$$P_{zA}(1) = Z_{A1}\, e^{-\zeta r_{A1}^2} \tag{5}$$

etc. and both Z_{A1} and Z_{B2} are increasingly positive in the same direction (see Fig. 1). The expectation values of the Hamiltonian,

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{1}{r_{12}} - \left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} + \frac{1}{r_{A2}} + \frac{1}{r_{B2}}\right) + \frac{1}{R} \tag{6}$$

is minimized with respect to ζ as well as the linear parameters α, β, and γ. The necessary basic integrals are tabulated in Table 1. At the infinite separation, the energy ia given by,

$$E_\infty = 2\left(-\frac{4}{3\pi}\right) = -0.848826\ (e^2/a_0) \tag{7}$$

with

$$\zeta_\infty = \frac{8}{9\pi} = 0.28294212 \tag{8}$$

Table 1. Atomic integrals

$$\langle S_A | S_B \rangle \equiv \int d\tau_1 \, S_{A1} S_{B1}$$

$$\langle S_A | \frac{1}{r_B} | S_B \rangle \equiv \int d\tau_1 \, S_{A1} \frac{1}{r_{B1}} S_{B1}$$

$$\langle S_A | K | S_B \rangle \equiv \int d\tau_1 \, S_{A1} \left(-\frac{\nabla_1^2}{2}\right) S_{B1}$$

$$[S_A S_C | S_B S_D] \equiv \iint d\tau_1 \, d\tau_2 \, S_{A1} S_{C1} \frac{1}{r_{12}} S_{B2} S_{D2}$$

$$\langle S_A | S_A \rangle = \left(\frac{\pi}{2\zeta}\right)^{\frac{3}{2}} \equiv N$$

$$\langle S_A | S_B \rangle = N e^{-\frac{\zeta}{2}R^2}$$

$$\langle P_{zA} | P_{zA} \rangle = \langle P_{xA} | P_{xA} \rangle = \langle P_{yA} | P_{yA} \rangle = N \cdot \frac{1}{4\zeta}$$

$$\langle P_{zA} | S_B \rangle = -\langle S_A | P_{zB} \rangle = N e^{-\frac{\zeta}{2}R^2} \cdot \frac{R}{2}$$

$$\langle P_{zA} | P_{zB} \rangle = N e^{-\frac{\zeta}{2}R^2} \cdot \frac{1}{4\zeta} (1 - \zeta R^2)$$

$$\langle P_{xA} | P_{xB} \rangle = \langle P_{yA} | P_{yB} \rangle = N e^{-\frac{\zeta}{2}R^2} \cdot \frac{1}{4\zeta} = \langle S_A | z_C^2 | S_B \rangle$$

$$\langle S_A | z_B^2 | S_B \rangle = \langle S_A | z_A^2 | S_B \rangle = N e^{-\frac{\zeta}{2}R^2} \cdot \frac{1}{4\zeta} (1 + \zeta R^2)$$

$$\langle S_A | \frac{1}{r_A} | S_A \rangle = \frac{\pi}{\zeta} \equiv L$$

$$\langle S_A | \frac{1}{r_B} | S_A \rangle = \langle S_B | \frac{1}{r_A} | S_B \rangle = L \cdot F(2\zeta R^2)$$

$$\langle S_A | \frac{1}{r_A} | S_B \rangle = \langle S_A | \frac{1}{r_B} | S_B \rangle = L e^{-\frac{\zeta}{2}R^2} \cdot F\left(\frac{\zeta R^2}{2}\right)$$

$$\langle S_A | \frac{1}{r_B} | P_{zA} \rangle = -\langle S_B | \frac{1}{r_A} | P_{zB} \rangle = L \cdot \frac{1}{4\zeta R} \left[F(2\zeta R^2) - e^{-2\zeta R^2} \right]$$

$$\langle P_{zA} | \frac{1}{r_A} | S_B \rangle = \langle P_{zA} | \frac{1}{r_B} | S_B \rangle = -\langle S_A | \frac{1}{r_A} | P_{zB} \rangle = -\langle S_A | \frac{1}{r_B} | P_{zB} \rangle$$

$$= L \cdot e^{-\frac{\zeta}{2}R^2} \cdot \frac{1}{2\zeta R} \left[e^{-\frac{\zeta}{2}R^2} + (\zeta R^2 - 1) F\left(\frac{\zeta R^2}{2}\right) \right]$$

$$\langle P_{zA} | \frac{1}{r_A} | P_{zA} \rangle = L \cdot \frac{1}{6\zeta}$$

Continuing Table I.

$$\langle p_{zA}|\frac{1}{r_B}|p_{zA}\rangle = \langle p_{zB}|\frac{1}{r_A}|p_{zB}\rangle = L\cdot\frac{1+2\gamma R^2}{8\gamma^2R^2}\left[F(2\gamma R^2)-e^{-2\gamma R^2}\right]$$

$$\langle p_{zA}|\frac{1}{r_A}|p_{zB}\rangle = \langle p_{zA}|\frac{1}{r_B}|p_{zB}\rangle$$
$$= L\,e^{-\frac{\gamma R^2}{2}}\cdot\frac{1}{8\gamma^2R^2}\left[-\left(1+\frac{\gamma R^2}{2}\right)e^{-\frac{\gamma R^2}{2}}+\left(1+\frac{\gamma R^2}{2}-\frac{\gamma^2R^4}{2}\right)\cdot F\left(\frac{\gamma R^2}{2}\right)\right]$$

$$\langle p_{xA}|\frac{1}{r_A}|p_{xB}\rangle = L\,e^{-\frac{\gamma R^2}{2}}\cdot\frac{1}{4\gamma^2R^2}\left[e^{-\frac{\gamma R^2}{2}}+(\gamma R^2-1)\cdot F\left(\frac{\gamma R^2}{2}\right)\right]$$

$$\langle p_{xA}|\frac{1}{r_B}|p_{xA}\rangle = L\cdot\frac{1}{16\gamma^2R^2}\left[e^{-2\gamma R^2}+(4\gamma R^2-1)\cdot F(2\gamma R^2)\right]$$

$$\langle s_{\gamma A}|K|s_{\gamma A}\rangle = \frac{3\gamma}{2}\langle s_{\gamma A}|s_{\gamma A}\rangle$$

$$\langle s_{\gamma A}|K|s_{\gamma B}\rangle = \frac{3\gamma}{2}\langle s_{\gamma A}|s_{\gamma B}\rangle\left(1-\frac{\gamma R^2}{3}\right)$$

$$\langle s_{\gamma A}|K|p_{zB}\rangle = -\langle p_{zA}|K|s_{\gamma B}\rangle = \frac{\gamma R}{4}\langle s_{\gamma A}|s_{\gamma B}\rangle(-5+\gamma R^2)$$

$$\langle p_{zA}|K|p_{zA}\rangle = \langle p_{xA}|K|p_{xA}\rangle = \langle p_{yA}|K|p_{yA}\rangle = \frac{5}{8}\langle s_{\gamma A}|s_{\gamma A}\rangle$$

$$\langle p_{zA}|K|p_{zB}\rangle = \frac{1}{8}\langle s_{\gamma A}|s_{\gamma B}\rangle(5-8\gamma R^2+\gamma^2R^4)$$

$$\langle p_{xA}|K|p_{xB}\rangle = \frac{1}{8}\langle s_{\gamma A}|s_{\gamma B}\rangle(5-\gamma R^2)$$

$$[s_{\gamma A}s_{\gamma A}|s_{\gamma A}s_{\gamma A}] = \frac{1}{4}\left(\frac{\pi}{\gamma}\right)^{\frac{5}{2}} \equiv M$$

$$[s_{\gamma A}s_{\gamma A}|s_{\gamma B}s_{\gamma B}] = M\,F(\gamma R^2)$$

$$[s_{\gamma B}s_{\gamma A}|s_{\gamma A}s_{\gamma B}] = M\,e^{-\gamma R^2}$$

$$[s_{\gamma A}p_{zA}|s_{\gamma B}p_{zB}] = [p_{zA}s_{\gamma A}|p_{zB}s_{\gamma B}] = \frac{M}{8\gamma^2R^2}\left[(1+\gamma R^2)e^{-\gamma R^2}-F(\gamma R^2)\right]$$

$$[p_{zA}s_{\gamma B}|p_{zB}s_{\gamma A}] = \frac{M}{24\gamma}\,e^{-\gamma R^2}\left[1-6\gamma R^2\right]$$

$$[p_{zA}p_{zA}|p_{zB}p_{zB}] = \frac{M}{32\gamma^2}\left[\left(2+\frac{2}{\gamma R^2}+\frac{3}{\gamma^2R^4}\right)F(\gamma R^2)\right.$$
$$\left.-\left(\gamma R^2+\frac{5}{2}+\frac{4}{\gamma R^2}+\frac{3}{\gamma^2R^4}\right)e^{-\gamma R^2}\right]$$

Continuing Table I.

$$[p_{zA}\, p_{zB} \mid p_{zB}\, p_{zA}] = \frac{M}{16\zeta^2} e^{-\zeta R^2}\left[\frac{49}{60} - \frac{5}{3}\zeta R^2 + \zeta^2 R^4\right]$$

$$[p_{zA}\, s_A \mid p_{zA}\, s_A] = \frac{M}{24\zeta}$$

$$[p_{zA}\, p_{zA} \mid p_{zA}\, p_{zA}] = \frac{49M}{960\zeta^2}$$

$$[p_{xA}\, s_A \mid p_{xB}\, s_B] = \frac{M}{16\zeta^2 R^2}\left[F(\zeta R^2) - e^{-\zeta R^2}\right]$$

$$[p_{xA}\, s_B \mid p_{xB}\, s_A] = \frac{M}{24\zeta} e^{-\zeta R^2}$$

$$[p_{zA}\, p_{xA} \mid p_{zB}\, p_{xB}] = \frac{M}{32\zeta^2}\left[e^{-\zeta R^2}\left(\frac{1}{2} + \frac{1}{\zeta R^2} + \frac{3}{2\zeta^2 R^4}\right) - \frac{3}{2\zeta^2 R^4} F(\zeta R^2)\right]$$

$$[p_{zA}\, p_{xB} \mid p_{zB}\, p_{xA}] = \frac{M}{320\zeta^2} e^{-\zeta R^2}\left[1 - \frac{10}{3}\zeta R^2\right]$$

$$[p_{xA}\, p_{xA} \mid p_{xB}\, p_{xB}] = \frac{M}{16\zeta^2}\left[e^{-\zeta R^2}\left(\frac{1}{8\zeta R^2} - \frac{9}{16\zeta^2 R^4}\right) + \left(1 - \frac{1}{2\zeta R^2} + \frac{9}{16\zeta^2 R^4}\right) \cdot F(\zeta R^2)\right]$$

$$[p_{xA}\, p_{yA} \mid p_{xB}\, p_{yB}] = \frac{3M}{256\zeta^4 R^4}\left[F(\zeta R^2) - \left(1 + \frac{2\zeta R^2}{3}\right) e^{-\zeta R^2}\right]$$

$$[p_{xA}\, p_{xB} \mid p_{xB}\, p_{xA}] = \frac{49M}{960\zeta^2} e^{-\zeta R^2}$$

$$[p_{xA}\, p_{yB} \mid p_{xB}\, p_{yA}] = \frac{M}{320\zeta^2} e^{-\zeta R^2}$$

Table 2 Parameters with ψ_o

$R(a_o)$	γ	$E(e^2/a_o)$	$\Delta E(e^2/a_o)^a$	$\Delta E(Kcal)^a$
.10	.76151172	7.70548393	8.55430993	5369.61733
.20	.74570703	2.72439126	3.57321726	2242.94063
.30	.72129297	1.08766927	1.93649527	1215.55551
.40	.69056055	.29332404	1.14215004	716.93786
.50	.65595117	-.16087390	.68795210	431.83373
.60	.61970703	-.44375001	.40507599	254.26984
.80	.54839063	-.75275100	.09607500	60.30714
1.00	.48451172	-.89458695	-.04576095	-28.72456
1.20	.43056055	-.95853735	-.10971135	-68.86680
1.40	.38629297	-.98294394	-.13411794	-84.18703
1.41	.38430664	-.98350874	-.13468274	-84.54157
1.42	.38235352	-.98402453	-.13519853	-84.86533
1.43	.38044922	-.98449281	-.13566681	-85.15928
1.44	.37849609	-.98491505	-.13608905	-85.42432
1.45	.37664063	-.98529266	-.13646666	-85.66135
1.46	.37473633	-.98562703	-.13680103	-85.87124
1.47	.37288086	-.98591947	-.13709347	-86.05481
1.48	.37107422	-.98617129	-.13734529	-86.21288
1.49	.36926758	-.98638374	-.13755774	-86.34623
1.50	.36743945	-.98655803	-.13773203	-86.45563
1.51	.36568359	-.98669534	-.13786934	-86.54182
1.52	.36392578	-.98679682	-.13797082	-86.60552
1.53	.36216797	-.98686357	-.13803757	-86.64743
1.54	.36045898	-.98689668	-.13807068	-86.66821
1.55	.35879883	-.98689720	-.13807120	-86.66853
1.56	.35708984	-.98686613	-.13804013	-86.64903
1.57	.35542969	-.98680446	-.13797846	-86.61032
1.58	.35381836	-.98671316	-.13788716	-86.55301
1.59	.35215820	-.98659314	-.13776714	-86.47767
2.00	.29985352	-.96555843	-.11673243	-73.27399
3.00	.25729297	-.89071068	-.04188468	-26.29139
4.00	.27039063	-.85699533	-.00816933	-5.12796
5.00	.27995117	-.84980647	-.00098047	-.61545
6.00	.28260938	-.84889366	-.00006766	-.04247
7.00	.28290234	-.84882888	-.00000288	-.00181
8.00	.28295117	-.84882641	-.00000041	-.00026
9.00	.28295117	-.84882636	-.00000036	-.00023
10.00	.28295117	-.84882636	-.00000036	-.00023

a. ΔE is the binding energy

Table 3 Parameters with Ψ_1

$R(a_o)$	ζ	α	$E(e^2/a_o)$	$\Delta E(e^2/a_o)^a$	$\Delta E(Kcal)^a$
.10	.76175586	-.14458238	7.69835710	8.54718310	5365.14376
.20	.74356055	-.10901606	2.72037720	3.56920320	2240.42097
.30	.71851172	-.05349848	1.08672523	1.93555123	1214.96293
.40	.69224414	.01939630	.29320564	1.14203164	716.86554
.50	.67004883	.11024470	-.16438811	.68443789	429.62783
.60	.65675586	.22487697	-.45654236	.39228364	246.23997
.80	.66714648	.56308911	-.80687782	.04194818	26.33125
1.00	.63175586	.78614495	-1.00391315	-.15508715	-97.34960
1.20	.53785352	.74985758	-1.09809010	-.24926410	-156.46532
1.40	.45156055	.65448691	-1.12983872	-.28101272	-176.39421
1.41	.44772461	.64958772	-1.13037724	-.28155124	-176.73225
1.42	.44396484	.64474192	-1.13083802	-.28201202	-177.02148
1.43	.44020508	.63985309	-1.13122359	-.28239759	-177.26351
1.44	.43649414	.63498751	-1.13153638	-.28271038	-177.45985
1.45	.43283203	.63014723	-1.13177875	-.28295275	-177.61199
1.46	.42921875	.62533414	-1.13195298	-.28312698	-177.72135
1.47	.42565430	.62055000	-1.13206130	-.28323530	-177.78935
1.48	.42208984	.61573825	-1.13210585	-.28327985	-177.81731
1.49	.41862305	.61101758	-1.13208872	-.28326272	-177.80656
1.50	.41519531	.60631904	-1.13201192	-.28318592	-177.75835
2.00	.28856055	.41343027	-1.08288700	-.23406100	-146.92220
3.00	.18834180	.20372119	-.93191204	-.08308604	-52.15385
4.00	.26319531	.03855085	-.85843964	-.00961364	-6.03457
5.00	.27965820	.01189570	-.84993441	-.00110841	-.69576
6.00	.28251172	.00776090	-.84894700	-.00012099	-.07595
7.00	.28290234	.00512190	-.84885209	-.00002609	-.01637
8.00	.28290234	.00344931	-.84883693	-.00001093	-.00686
9.00	.28295117	.00242331	-.84883155	-.00000555	-.00349
10.00	.28295117	.00176681	-.84882912	-.00000312	-.00196

a. ΔE is the binding energy

Table 4 Parameters with ψ_2

$R(a_o)$	ζ	β	γ	$E(e^2/a_o)$	$E(e^2/a_o)^a$ Δ	$E(Kcal)^a$ Δ
.10	.76470703	-.13959827	-.15117224	7.68241372	8.53123972	5355.13595
.20	.74639063	-.10390419	-.14889603	2.70452484	3.55335084	2230.47030
.30	.72129297	-.04821112	-.14564331	1.07102056	1.91984656	1205.10496
.40	.69490234	.02486938	-.14195733	.27170598	1.12653138	707.13389
.50	.67239063	.11573707	-.13833205	-.17961590	.66921010	420.06920
.60	.65860938	.22993692	-.13513166	-.47139298	.37743303	236.91811
.80	.66619531	.56168610	-.12842102	-.82022224	.02860376	17.95484
1.00	.62934180	.77913363	-.11031170	-1.01472434	-.16589834	-104.13588
1.20	.53590234	.74368853	-.08975594	-1.10692240	-.25809640	-162.00943
1.40	.45004883	.64949613	-.07371004	-1.13725586	-.28842986	-181.05002
1.41	.44621094	.64462184	-.07302137	-1.13773406	-.28890806	-181.35019
1.42	.44245117	.63980411	-.07234414	-1.13813537	-.28930937	-181.60210
1.43	.43869141	.63494326	-.07167428	-1.13846226	-.28963626	-181.80729
1.44	.43502930	.63016791	-.07101656	-1.13871718	-.28989118	-181.96730
1.45	.43136719	.62535533	-.07036593	-1.13890245	-.29007645	-182.08360
1.46	.42775391	.62057020	-.06972471	-1.13902034	-.29019434	-182.15760
1.47	.42423828	.61587370	-.06909522	-1.13907307	-.29024707	-182.19070
1.48	.42072266	.61114773	-.06847242	-1.13906275	-.29023675	-182.18422
1.49	.41725586	.60645405	-.06785865	-1.13899146	-.29016546	-182.13947
1.50	.41380469	.60175529	-.06725211	-1.13886121	-.29003521	-182.05771
2.00	.28756055	.41043144	-.04534442	-1.08771306	-.23888706	-149.95156
3.00	.18704883	.20274546	-.02644097	-.93446648	-.08564048	-53.75730
4.00	.26229297	.03857546	-.01467480	-.85886068	-.01003468	-6.29886
5.00	.27948828	.01185844	-.00714252	-.85002611	-.00120011	-.75332
6.00	.28243945	.00775276	-.00408606	-.84897658	-.00015058	-.09452
7.00	.28285352	.00511993	-.00257283	-.84886379	-.00003779	-.02372
8.00	.28290234	.00344842	-.00172458	-.84884219	-.00001619	-.01016
9.00	.28295117	.00242296	-.00121149	-.84883415	-.00000815	-.00511
10.00	.28295117	.00176566	-.00088333	-.84883050	-.00000450	-.00282

a. ΔE is the binding energy

That is, E_{∞} is twice the variational energy of the hydrogen atom with 1s Gaussian function. We define the binding energy, ΔE, at an internuclear separation R with the optimized energy at the separation minus E_{∞}. The results are given in Tables 2, 3, and 4.

3. Discussion

In Fig. 2, we plot the binding energies obtained together with the most likely one. The binding energies at the calculated equilibrium separations are: $\Delta E(\psi_0)$ =-86.67 kcal/mol at Req=1.55a_0, $\Delta E(\psi_1)$ =-177.82 kcal/mol at Req=1.48a_0, and $\Delta E(\psi_2)$ =-182.19 kcal/mol at Req=1.47a_0. That is, $\Delta E(\psi_1)$ and $\Delta E(\psi_2)$ overshoot the exact one, -109.32 kcal/mol, and $\Delta E(\psi_0)$ undershoots the exact one near the equilibrium separation (exact Req=1.40a_0). However, it is noteworthy that the Gaussian functions approximate the true energy more closely near the equilibrium separation than at the infinite separation. Indeed, $E(\psi_1)$ is -710.6 kcal/mol, and $E(\psi_2)$ is -715.0 kcal/mol, while the correct value is -737.0 kcal/mol. On the other hand, the Gaussians give -531.8 kcal/mol, for the energy of two infinitely separated hydrogen atoms while the correct value is -627.7 kcal/mol. The fact is in contrast to the case of Slater-type functions in which the energy is exactly given at the infinite separation and approximately at the finite separation.

Although the introduction of the polarization term in the z direction, p_z function, leads to the substantial energy improvement near the equilibrium separation, the addition of p_x and p_y functions gives very little additional influence to the overall picture of the

potential curve. As the two hydrogen atoms recede from each other, $\Delta E(\psi_1)$ sharply decreases in magnitude and crosses the exact value near $R=3.4a_0$, and joins quickly to the asymptotic (zero) line.

The polarization parameter α of ψ_1 (see Fig. 3) has the maximum value near $R=1.0a_0$. The positive value of α at $R > 0.4a_0$ implies the instantaneous mutual polarization of the two hydrogen atoms which arises because the electrons repel one another. In the case of the Slater-type functions, the corresponding parameter is positive at $R > 4.1a_0$. The striking difference may be attributed to the highly concentrated charge density of the Gaussian description near the nuclei. Furthermore the ratio β/γ of ψ_2 converges to the assymptotic value -2 near $R=7a_0$, while the ratio of the Slater-type counterpart attains the same value near $R=10a_0$ (see Fig. 4).

Thus, the Gaussian counterpart of the Hirschfelder-Linnett function

(a) is fairly good approximation near the equilibrium separation of the hydrogen molecule, but

(b) is not suitable for the description of the long-range behavior.

The facts could be a guide when one uses the Gaussian basis set for the many-center calculation. In another words, there is optimum separation between centers for the economy of the number of the Gaussian-type basis functions.

When one is interested in the functional dependence of the interaction energy of the two hydrogen atoms at long range, one need not confine oneself to the true units of the energy and length.

Since the integrals arises from the Gaussian are all simple forms, it may be a reasonable attempt to seek certain empirization which would give plausible potential curve. For instance, by adjusting atomic unit of the energy and length, one can fit the equilibrium separation and the corresponding binding energy to those of the true values. However, it turns out that the potential curves so obtained still approaches to the assymptotic line too quickly (see Fig. 5 and Fig. 6). Thus we conclude that the Gaussian functions are inadequate for the descriptions of the long range behavior unless drastic remedy is applied through severe empirization or use of the large basis set.

References and Footnotes

1. S.F. Boys, Proc. Roy. Soc. (London) A200, 542 (1950).

2. L.C. Allen, J. Chem. Phys. 37, 200 (1962).

3. A. Dalgarno and J.T. Lewis, Proc. Phys. Soc. (London), A69 57 (1956).

4. J.O. Hirschfelder and P.O. Lowdin, Mol. Phys. 2, 229 (1959), ibid 9, 491 (1966).

5. W. Kolos and C.C.J. Roothaan, Rev. Mod. Phys. 32, 219 (1960).

6. R.J. Bell, Proc. Phys. Soc. (London) A86, 239 (1965).

7. J.O. Hirschfelder and J.W. Linnett, J. Chem. Phys. 18, 130 (1950).

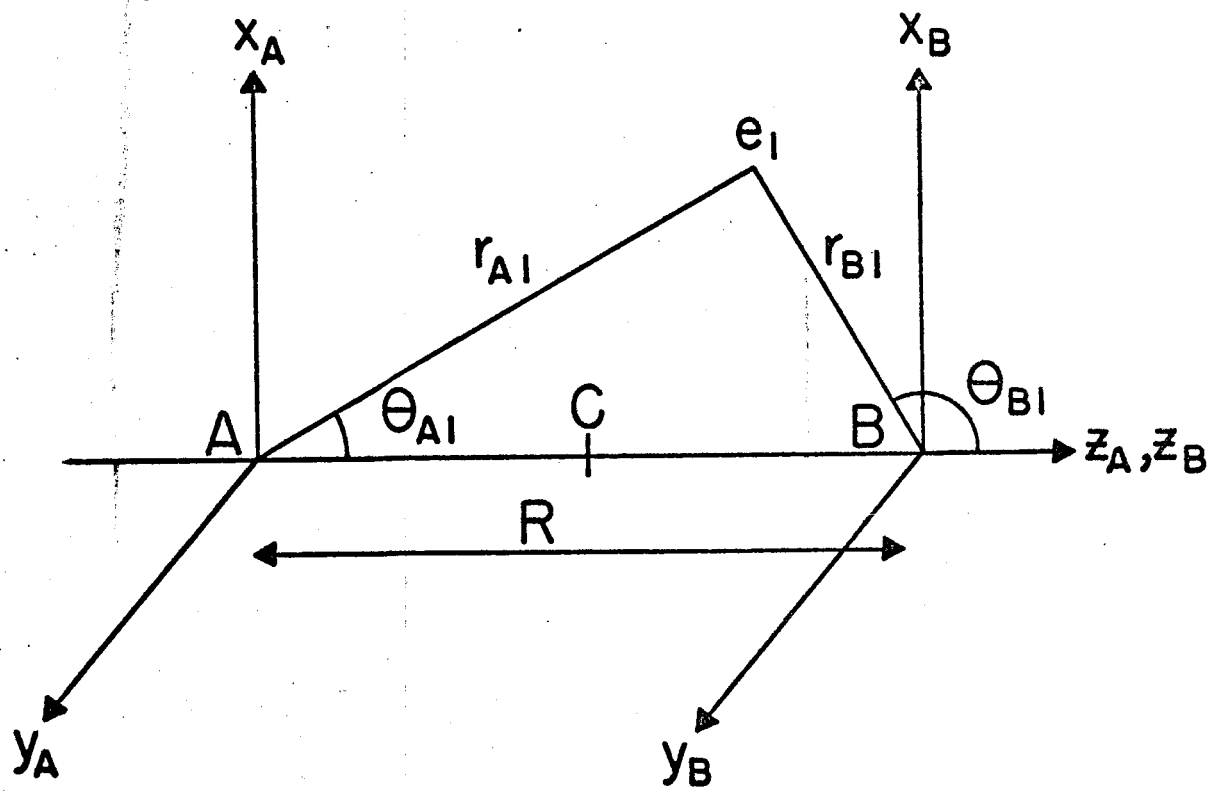

Figure 1. The coordinate system. C is the internuclear mid-point.

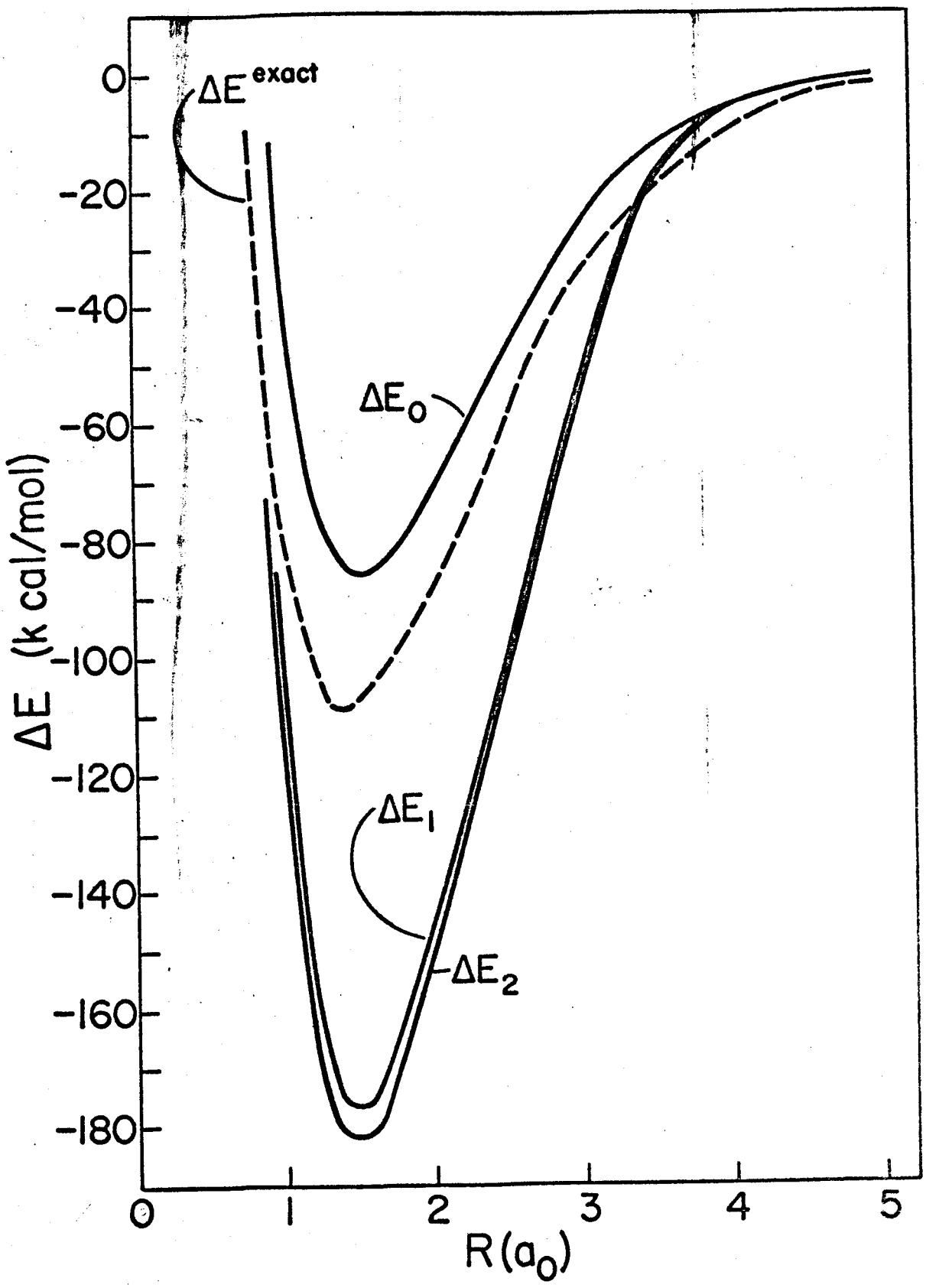

Fig. 2 The binding energies

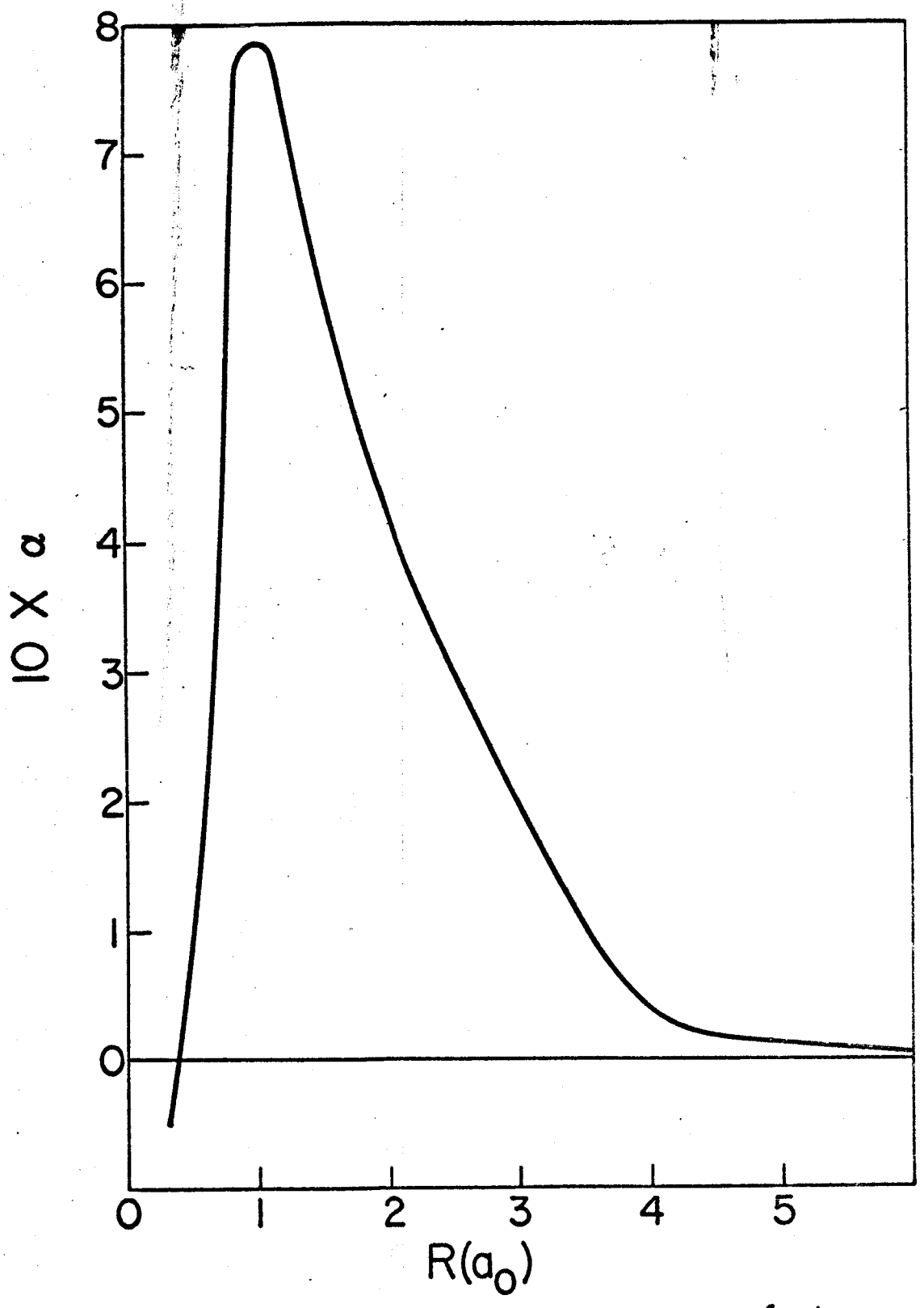

Fig. 3 Z-polarization parameter α of ψ

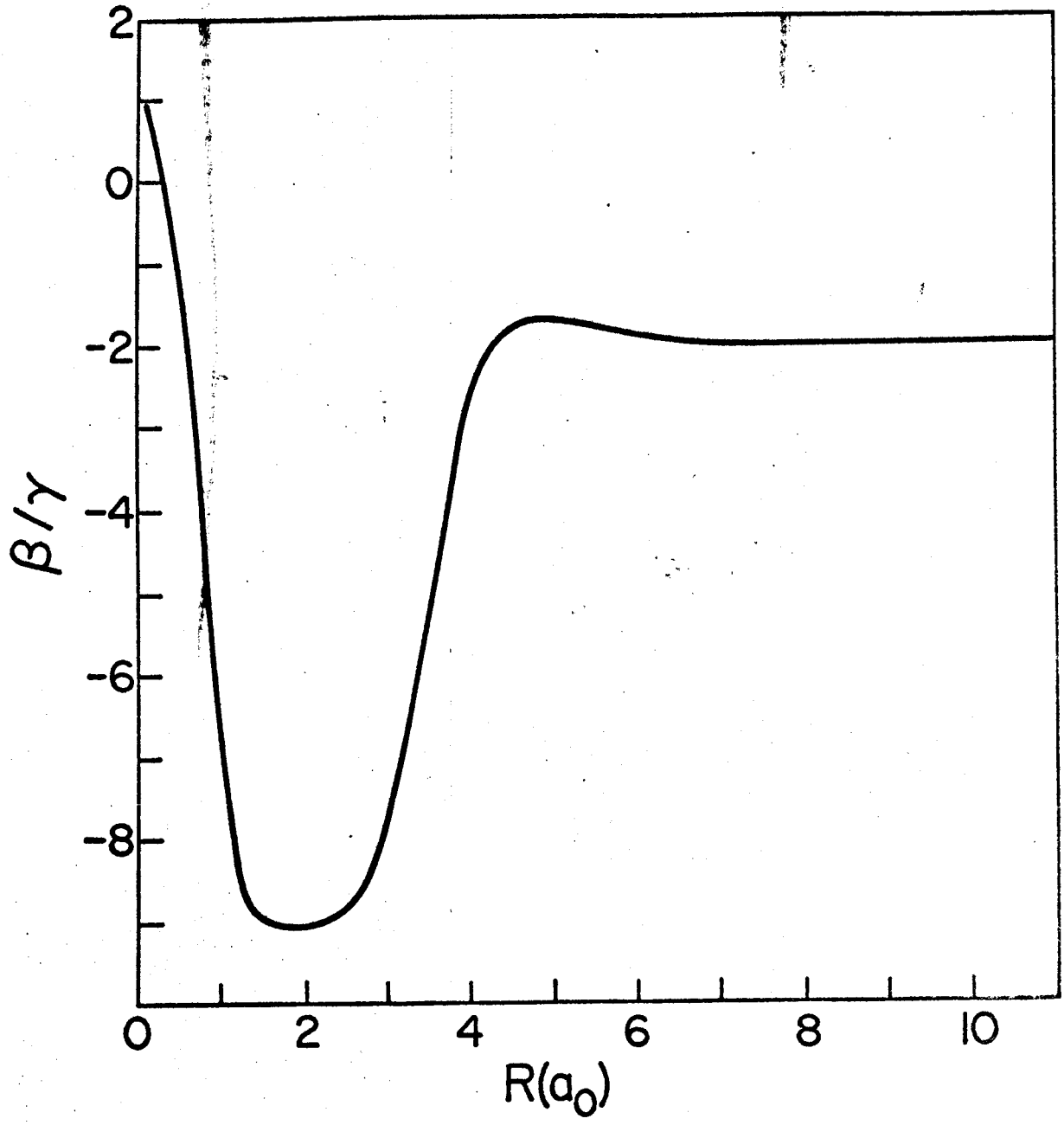

Fig. 4 The ratio β/γ of ψ_2

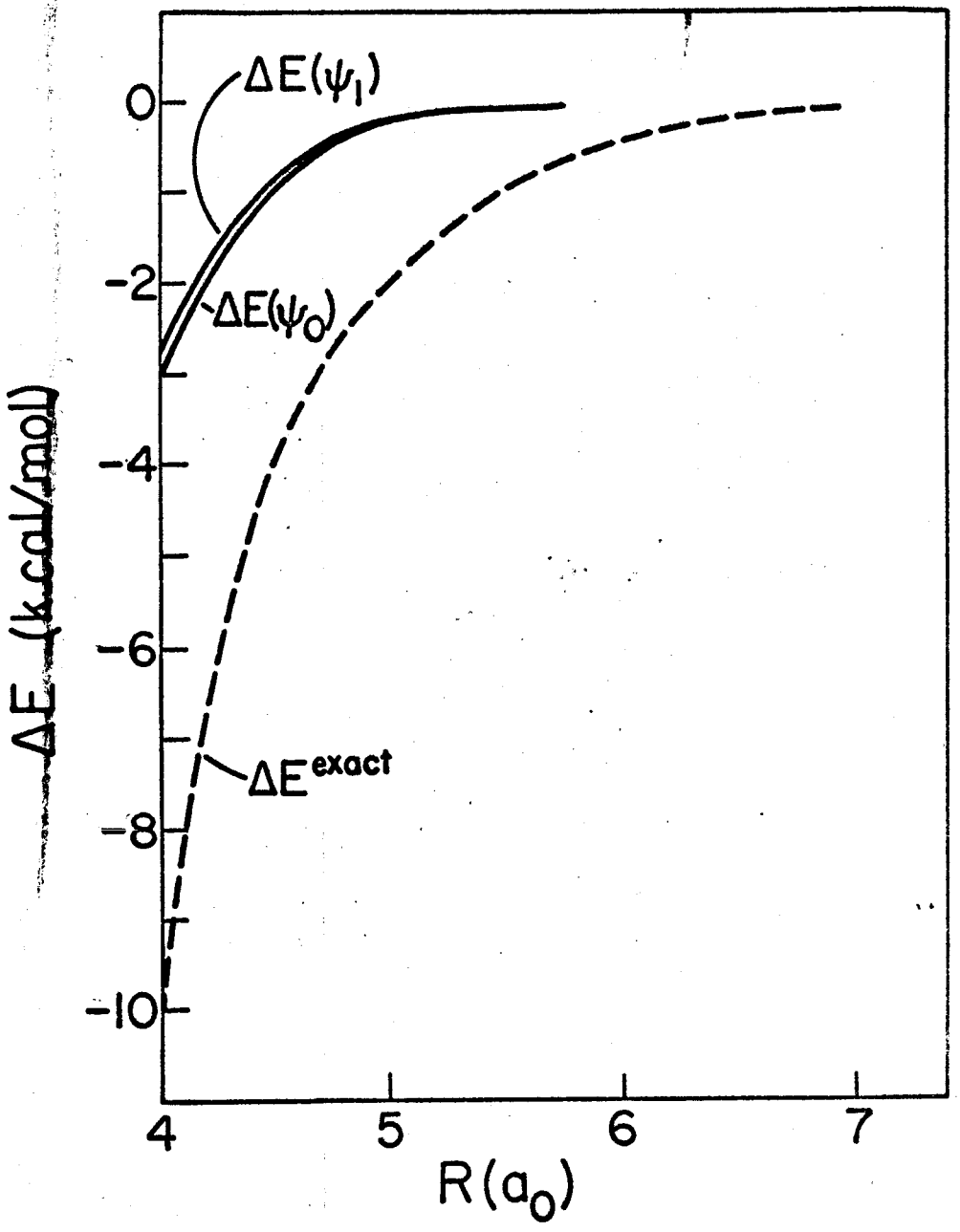

Fig. 6 Potential curve with adjusted units