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Peculiarity of the Dickinson H_2^+ wave function

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According to the zero potential energy criterion proposed recently, the Dickinson wave function for the $2p\sigma_u$ state of the H_2^+ system is an unexpectedly poor approximation so long as the known parameters are employed. We re-examine the optimum parameters for the Dickinson wave function and find that there exist two sets of optimum parameters with different wave function characteristics. The corresponding energy curves cross at $R = 1.91$ a.u., though the difference is very small. We suggest that a new set of optimum parameters with slightly higher energy for $R > 1.91$ a.u. is more acceptable physically than the previously reported set.

Key words: Dickinson function — H_2^+ system — Zero potential energy

1. Introduction

In a recent paper [1], the zero potential energy criterion (E_{zp}), which is a possible partner to the zero momentum energy criterion (E_{zm}) [2, 3], has been proposed as a measure for assessing the accuracy of approximate wave functions. Applications of E_{zp} for several approximate wave functions of the H_2^+ molecule have revealed that it is a very sensitive and effective criterion to appraise the accuracy of wave functions. In the ground $1s\sigma_g$ state, the accuracy of approximate wave functions assessed by E_{zp} has been almost parallel to the one anticipated by the corresponding energy expectation values, but in the first excited $2p\sigma_u$ state, this tendency has not been found. Surprisingly, the Dickinson wave function, which incorporates the $2p\sigma$ polarization function (with exponent ζ_p) in the minimal $1s$ basis (with exponent ζ_s), has shown a worse behavior than that of the simple LCAO wave function of 1s AO's, so long as we employ the parameter values reported in previous papers [4, 5]. Furthermore, the zero potential energy criterion unexpectedly concludes that the wave function obtained by the constrained optimization [6] $\zeta_s = \zeta_p$ (Dickinson-*a* wave function in [1]) is superior to the one obtained by the independent variation of ζ_s and ζ_p (Dickinson-*b* wave function in [1]).

The purpose of this paper is to investigate these peculiarities of the Dickinson H_2^+ wave function for the $2p\sigma_u$ state and to assign the most acceptable parameters. We first examine the energy surface of the system as a function of the exponents ζ_s and ζ_p at the nuclear separation $R = 2.0$ a.u. As a result, we find that there exist two local energy minima with different values of the parameters. One, which corresponds to the parameters reported previously, has an inwardly polarized electron distribution, while the other, which is newly found and slightly unfavorable energetically, has an outwardly polarized electron distribution. The zero potential energy criterion suggests the adequacy of the latter as an approximate wave function for the $2p\sigma_u$ state (Sect. 2). The physical acceptability of the new wave function is further supported by the comparison with the exact wave function and by the local energy consideration (Sect. 3). Atomic units are used throughout this paper.

2. Two energy minima in the $2p\sigma_u$ state

The normalized Dickinson wave function for the $2p\sigma_u$ state of H_2^+ is given by [4–6],

$$\psi(\boldsymbol{r}) = (2 + 2c^2 - 2S)^{-1/2}\{[(1s)_a + c(2p\sigma)_a] - [(1s)_b - c(2p\sigma)_b]\}, \tag{1}$$

where

$$S = S_{ss} - 2cS_{sp} + c^2 S_{pp}, \tag{2a}$$

$$S_{ss} = \int (1s)_a(1s)_b \, d\boldsymbol{r}, \tag{2b}$$

$$S_{sp} = \int (1s)_a(2p\sigma)_b \, d\boldsymbol{r}, \tag{2c}$$

$$S_{pp} = \int (2p\sigma)_a(2p\sigma)_b \, d\boldsymbol{r}, \tag{2d}$$

and $(1s)_a$ and $(2p\sigma)_a$ denote hydrogenic orbitals on the nucleus a with exponents ζ_s and ζ_p, respectively. The orbitals $(1s)_b$ and $(2p\sigma)_b$ have analogous meaning, but we use the common z-axis pointing from a to b for $(2p\sigma)_a$ and $(2p\sigma)_b$. The Dickinson wave function (Eq. (1)) contains three variational parameters ζ_s, ζ_p, and c, the last being the mixing coefficient.

At the internuclear distance $R = 2.0$, the contour map of the electronic energy E is shown in Fig. 1 as a function of the two exponents. In this case, the remaining parameter c is variationally determined for given ζ_s and ζ_p. In Fig. 1, it is very clear that there are two local minima of energy (labelled by A and B) in the parameter space. The properties of these minima are compared in Table 1. The

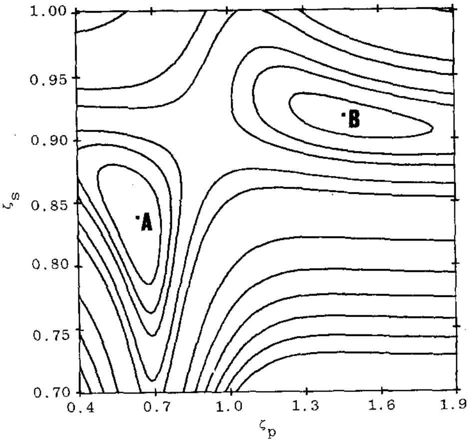

Fig. 1. Contour map of the Dickinson electronic energy for the $2p\sigma_u$ state of the H_2^+ molecule at $R=2.0$. Contour values are -0.6664, -0.6662, -0.6660, -0.6655, $-0.6650(0.0025)-0.6500$ from the innermost curves surrounding the minima A and B

minimum A corresponds to the already-known parameters, whereas the minimum B (its energy is higher than A only by 0.000120 a.u.) is newly found in this study. The notable difference between the two is that the minimum A has a positive c and hence an electron distribution polarized inwardly but the minimum B has a negative c leading to an electron distribution polarized outwardly. The latter seems reasonable judging from the antibonding nature of the $2p\sigma_u$ state. This is also supported by the zero potential energy values: The comparison of E_{zp}'s at $R=2.0$ (Table 1) shows that the minimum B has a closer value to the exact one than the minimum A. The E_{zp} of the minimum B also occupies a proper position in Table III of [1], in which energy expectation values together with E_{zp}'s of various approximate wave functions with different levels of accuracy were compared. These two minima are also examined at various values of R as summarized in Table 2. We see that the trends observed at $R=2.0$ remain unaltered. From Table 2, it can be seen that the corresponding two energy curves cross at $R_c \sim 1.91$, though the difference is rather small for $R>1.5$. The trajectories of the two exponents ζ_s and ζ_p are shown in Fig. 2 as a function of R. It is understood that these trajectories neither join nor cross. Namely the two minima are characterized by the positivity and negativity of the parameter c for the whole range of R, and

Table 1. Comparison of the two energy minima in the $2p\sigma_u$ state of the H_2^+ molecule at $R=2.0$

	Minimum A	Minimum B	Exact
E	−0.666597	−0.666477	−0.667534[a]
c	+0.050341	−0.029593	—
ζ_s	0.835572	0.916083	—
ζ_p	0.632507	1.457379	—
E_{zp}	−0.200032	−0.419604	−0.667534[b]

[a] [7]
[b] [1]

Table 2. Two sets of optimized parameters and electronic energies of the Dickinson wave function for the $2p\sigma_u$ state of the H_2^+ molecule

	Dickinson function with positive c				Dickinson function with negative c				Energy
R	c	ζ_s	ζ_p	$-E$	c	ζ_s	ζ_p	$-E$	difference
0.6	0.030964	0.398567	0.391144	0.493153	−0.557194	0.746769	1.053422	0.524170	−0.031017
0.8	0.044417	0.441624	0.436537	0.523261	−0.379197	0.772910	1.090049	0.542353	−0.019092
1.0	0.055605	0.504799	0.483990	0.553231	−0.262275	0.798180	1.131974	0.564038	−0.010807
1.2	0.064109	0.573030	0.530895	0.581900	−0.179212	0.822191	1.177545	0.587444	−0.005544
1.4	0.066714	0.647061	0.571398	0.608179	−0.119299	0.845498	1.228425	0.610701	−0.002522
1.6	0.063274	0.719749	0.600950	0.631273	−0.077126	0.869079	1.288700	0.632232	−0.000959
1.8	0.056753	0.783698	0.619832	0.650770	−0.048501	0.892955	1.362994	0.650987	−0.000217
1.9095[a]	0.053090	0.813630	0.627195	0.659882	−0.037168	0.905795	1.411616	0.659882	0.000000
2.0	0.050341	0.835572	0.632507	0.666597	−0.029593	0.916083	1.457379	0.666477	0.000120
2.2	0.045618	0.875714	0.644016	0.678948	−0.017234	0.937245	1.585110	0.678678	0.000270
2.4	0.042909	0.905987	0.657766	0.688172	−0.009174	0.955697	1.785368	0.687838	0.000334
2.6	0.041950	0.928531	0.674893	0.694689	−0.004069	0.971290	2.204363	0.694330	0.000359
2.8	0.042223	0.945328	0.694494	0.698927	−0.001489	0.984338	3.095189	0.698560	0.000367
3.0	0.043151	0.958012	0.714685	0.701284	−0.000515	0.994686	4.412556	0.700909	0.000375
3.2	0.044263	0.967780	0.733841	0.702113	−0.000191	1.002393	5.956452	0.701722	0.000391
3.4	0.045271	0.975428	0.751126	0.701716	−0.000078	1.007933	7.582468	0.701301	0.000415
3.6	0.046038	0.981479	0.766343	0.700347	−0.000034	1.011776	9.333265	0.699904	0.000443
3.8	0.046518	0.986284	0.779619	0.698218	−0.000016	1.014306	11.259789	0.697745	0.000473
4.0	0.046718	0.990098	0.791193	0.695501	−0.000007	1.015829	13.406610	0.695001	0.000500

[a] The two energy curves cross at this R value

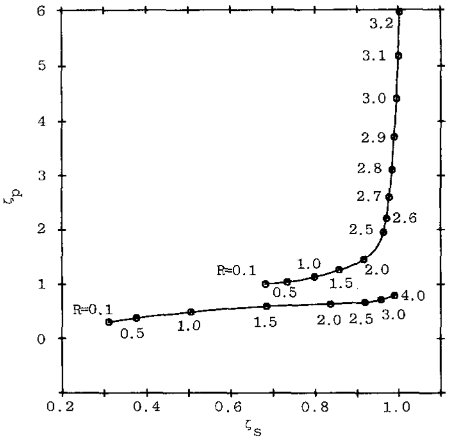

Fig. 2. Trajectories of the two set of the optimized exponents ζ_s and ζ_p as a function of R

hence we hereafter use the subscripts + and − to distinguish the properties accompanied with them. In what follows, the propriety of the two wave functions to describe the $2p\sigma_u$ state will be examined through the contour maps of wave functions $\psi(\boldsymbol{r})$ and local energies $\varepsilon(\boldsymbol{r})$.

3. Comparison of wave functions and local energies

The wave functions ψ_+ and ψ_- at $R = 2.0$ are illustrated in Fig. 3 as well as the exact one ψ_e [7]. We first compare the wave functions ψ_+ and ψ_e: Their behaviors are similar to each other within a circle with the radius 6 centered on the midpoint of the nuclei. However, the deviation becomes larger as the radius increases and a nodal surface appears in ψ_+ at the radius 8 or so, which never occurs in ψ_e. The phase of ψ_+ becomes opposite outside this surface, and the wave function ψ_+ represents itself a property of the $3p\sigma_u$ state. Next we compare the wave functions ψ_- and ψ_e: Their behaviors quite resemble one another within a circle

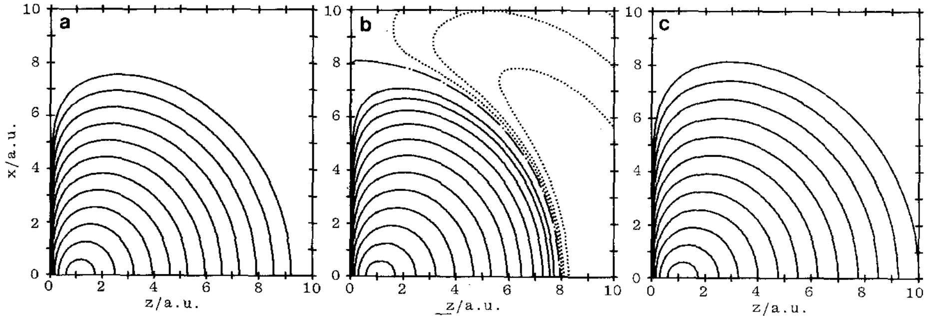

Fig. 3a–c. Quadrant comparison of the $2p\sigma_u$ wave functions $\psi_e(x, 0, z)$, $\psi_+(x, 0, z)$, and $\psi_-(x, 0, z)$ at $R = 2.0$. Positive values (*solid lines*) are 2^{-n} ($n = 2, 3, \ldots, 13$) and negative values (*dotted lines*) are $-2^{-n} \times 10^{-3}$ ($n = 3, 4, 5$). The chain line in **b** is the contour of zero value. **a** $\psi_e(x, 0, z)$; **b** $\psi_+(x, 0, z)$; **c** $\psi_-(x, 0, z)$

of the radius 4 and the contour maps almost overlap in this region. Beyond this radius, the difference increases gradually, and ψ_- has a larger amplitude than ψ_e in the long range tail. Nevertheless, the wave function ψ_- does *not* have any superfluous nodes (except for the node bisecting the bond) as found in ψ_+. Thus the wave function ψ_- is favorable, at least qualitatively, than ψ_+.

Secondly, we compare the local energy maps. Let the Hamiltonian of the system be $H(\boldsymbol{r})$. Then the local energy $\varepsilon(\boldsymbol{r})$ is defined by [8]

$$\varepsilon(\boldsymbol{r}) = [H(\boldsymbol{r})\psi(\boldsymbol{r})]/\psi(\boldsymbol{r}). \tag{3}$$

If $\psi(\boldsymbol{r})$ is an exact eigenfunction of $H(\boldsymbol{r})$, $\varepsilon(\boldsymbol{r})$ is nothing but its eigenvalue and independent of $\boldsymbol{r}$. In the case of an approximate $\psi(\boldsymbol{r})$, the local energy $\varepsilon(\boldsymbol{r})$ is no longer a constant and fluctuates as $\boldsymbol{r}$ varies. The degree of fluctuation then reflects directly the accuracy of the wave function considered. The zero potential energy E_{zp} employed in Sect. 2 is defined as

$$E_{zp} = \lim_{\boldsymbol{r}\to\infty} \varepsilon(\boldsymbol{r}), \tag{4}$$

in the present case.

Comparison of the contour maps of local energies ε_+ and ε_-, corresponding to ψ_+ and ψ_- respectively, is presented in Fig. 4 for $R = 2.0$. At the nuclear positions ($x = y = 0$, $z = \pm 1.0$), both of ε_+ and ε_- diverge towards a positive infinity. The ε_+ map also contains an additional divergence on the surface corresponding to the superfluous node discussed above. It is readily observed from Fig. 4 that ε_+ map is full of variety compared with ε_- map: Indeed, the intervals of the contour lines are narrower in ε_+ and even positive values happen. These observations mean that ψ_+ is a very poor approximate wave function. In view of these facts, it can be said that the wave function ψ_- which yields the less $\boldsymbol{r}$-dependent ε_- is better than ψ_+.

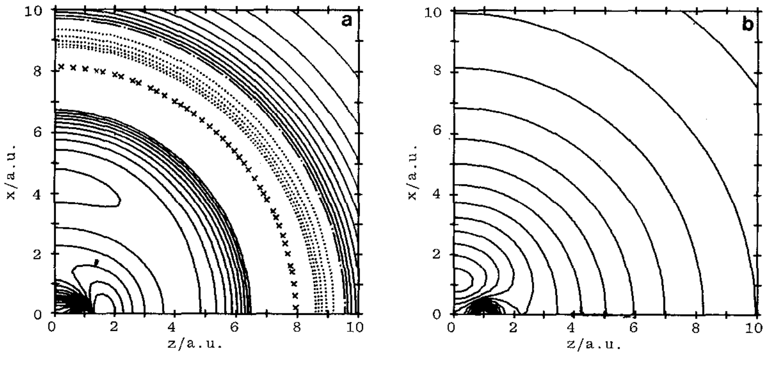

Fig. 4a,b. Quadrant comparison of the local energy contour maps $\varepsilon_+(x, 0, z)$ and $\varepsilon_-(x, 0, z)$ at $R = 2.0$. Positive values (*dotted lines*) are 0.1(0.1)0.5 and negative values (*solid lines*) are −0.8(0.02)−0.02. In **a**, the chain line corresponds to zero, and the cross marks represent the divergent (discontinuous) region. In **b**, the contours with −0.80, −0.78, and −0.76 do not appear. **a** $\varepsilon_+(x, 0, z)$; **b** $\varepsilon_-(x, 0, z)$

4. Conclusion

The Dickinson wave function for the $2p\sigma_u$ state of H_2^+ has been found to have a peculiarity that there exist two energy minima with respect to the two exponents involved. The corresponding wave functions have quite different characteristics. Detailed examinations of the contour maps for the wave functions ψ_+ and ψ_-, and the local energies ε_+ and ε_-, as well as the associated zero potential energies, suggest that the newly found energy minimum and wave function are more physically acceptable as the $2p\sigma_u$ state than those hitherto believed. If one strongly insists on the variational principle, he may claim that our conclusion is wrong, since the new wave function has a slightly higher energy (for some R-region) than the already-known wave function. However, we can cite a few sentences from Lesk's physical chemistry text [9]; "The wave function that corresponds to the best approximation to the energy may not be the best approximation to the wave function. It need not give the best approximation to properties other than the (ground state) energy." (See also [10].)

The Dickinson wave function for the H_2^+ system represents the simplest case of a familiar technique of the inclusion of polarization functions into the minimal basis set to improve the wave function. Nevertheless, the present study shows that the appropriate choice of parameters is not so straightforward, and suggests that one should be careful particularly to the exponents of additional polarization functions in the general quantum-chemical calculations.

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