

Application of hyper-spheroidal coordinates to HD⁺

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Abstract

By adopting hyper-spheroidal coordinates, the hyper-radial adiabatic potential energy curves with correct asymptotic energies are obtained for the HD⁺ molecular ion. Vibrational-rotational energies are also calculated for the lowest potential energy curve.

1. Introduction

The conventional Born-Oppenheimer approximation for diatomic molecules does not give correct dissociation energies. Pack¹⁾ and Struensee et al²⁾ proposed an "improved adiabatic" (IA) approximation for HD⁺ and dtu⁺. It includes the relative angular momentum of the nuclei in the adiabatic Hamiltonian. In their approach, the relative angular momentum of the nuclei and the diagonal non-adiabatic interaction lead to the symmetry breaking effects due to the unequal masses of the two nuclei. Macek and Jerjian³⁾ and recently Jerjian and Macek⁴⁾ applied hyper-spherical coordinates to HD⁺ because this coordinate system automatically gives the correct dissociation limits. They have solved, neglecting those parts of the Coulomb interaction which are of the order of the ratio of the electron mass m_e to the proton mass M_p , the eigenvalue problem of the Hamiltonian adiabatically in terms of the hyper-radius. They obtained potential energy curves which have the correct dissociation energies. Using the approximate hyper-radial adiabatic $1\sigma_g$ potential curve obtained as described above, they calculated the vibrational energies of HD⁺ without taking account of the diagonal non-adiabatic coupling.

In hyper-radial coordinates, five variables other than the hyper-radius can be chosen in many ways. Spheroidal coordinates are the most natural coordinate with which to study diatomic molecules in the adiabatic approximation. Therefore, the spheroidal coordinates associated with the hyper-radius, which is called "hyper-spheroidal coordinates", must be one of the best choice to treat three body diatomic molecules in the hyper-radial adiabatic approximations. In a recent letter⁵⁾, we have demonstrated that hyper-spheroidal coordinates work very well for the bound state problem of the dtu⁺ molecule. Here, we investigate HD⁺ in hyper-spheroidal coordinates. In these coordinates, the adiabatic Hamiltonian is represented in a tractable form. Therefore, it is possible to calculate the eigenfunctions and eigenvalues of the adiabatic Hamiltonian accurately without neglecting any interactions or without introducing any further approximation.

2. Formulation.

The Schroedinger equation for the HD⁺ system is given by

$$[H - E] \Psi(\mathbf{x}, \mathbf{X}) = 0, \quad (1)$$

where

$$H = -\frac{1}{2M} \nabla_{\mathbf{X}}^2 - \frac{1}{2m} \nabla_{\mathbf{x}}^2 + V(\mathbf{x}, \mathbf{X}), \quad (2)$$

is the total Hamiltonian, E the total energy, and Ψ the total wavefunction. M and m are the reduced masses for the proton p and deuteron d system and of the $(p + d)$ and electron e system, respectively, thus

$$1/M = 1/M_p + 1/M_d, \quad (3)$$

and

$$1/m = 1/m_e + 1/(M_p + M_d). \quad (4)$$

In Eqs. (1) and (2), X represents the position vector of d relative to p , x that of the electron e with respect to the centre of mass of $(p+d)$ (see Fig. 1) and V the Coulomb interactions between the three particles,

$$V = 1/X - 1/r_p - 1/r_d. \quad (5)$$

Atomic units are used throughout this paper unless otherwise stated, that is

$$e = \hbar = m_e = 1. \quad (6)$$

The hyper-radius R for the system is defined by

$$M_0 R^2 = M X^2 + m x^2, \quad (7)$$

where M_0 is an arbitrary mass constant. We choose $M_0 = M$ in the following. By using the hyper-radius so defined, the total Hamiltonian reduces to the following form⁶⁾

$$H = -\frac{1}{2M} \frac{1}{R^5} \frac{\partial}{\partial R} R^5 \frac{\partial}{\partial R} + h(\Omega; R), \quad (8)$$

where h is the adiabatic Hamiltonian operator which includes R as a parameter and Ω represents five dimensionless variables. In hyper-spheroidal coordinates, Ω is a set of variables $(\xi, \eta, \varphi; \hat{X})$, where \hat{X} is the unit vector along X . The variables ξ and η are defined in terms of the previously defined variables as

$$\xi = (r_p + r_d)/X, \quad \eta = (r_p - r_d)/X. \quad (9)$$

The angle φ is the azimuthal angle of x around the \hat{X} direction. These are the spheroidal coordinates for x . With these variables, h can be written as

$$h = -\frac{\rho^2}{2m} \nabla_r^2 + \frac{\rho}{2MR^2} (\hat{J}^2 - 2\hat{J} \cdot \hat{l}) + V + \frac{\rho \hat{q}}{MR^2}, \quad (10)$$

where

$$\nabla_r^2 = \frac{4}{R^2} \left[\frac{1}{(\xi^2 - \eta^2)} \left\{ \frac{\partial}{\partial \xi} (\xi^2 - 1) \frac{\partial}{\partial \xi} + \frac{\partial}{\partial \eta} (1 - \eta^2) \frac{\partial}{\partial \eta} \right\} + \frac{1}{(\xi^2 - 1)(1 - \eta^2)} \frac{\partial^2}{\partial \varphi^2} \right], \quad (11)$$

$$\hat{l} = -i \mathbf{x} \times \nabla_{\mathbf{x}}, \quad (12)$$

$$\rho = 1 + mx^2 / MX^2 = 1 + \frac{m}{4M} (\xi^2 + \eta^2 - 1 - 2\kappa\xi\eta + \kappa^2) \quad (13)$$

$$\hat{q} = \frac{1}{(\xi^2 - \eta^2)} \left[(\xi - \kappa\eta) (\xi^2 - 1) \frac{\partial}{\partial \xi} + (\eta - \kappa\xi) (1 - \eta^2) \frac{\partial}{\partial \eta} \right], \quad (14)$$

$$\kappa = (M_d - M_p) / (M_p + M_d), \quad (15)$$

$$V = 1/X - 1/r_p - 1/r_d = \frac{\sqrt{\rho}}{R} \left(1 - \frac{4\xi}{\xi^2 - \eta^2} \right) \quad (16)$$

and \hat{J} is the total angular momentum operator. As discussed by Matveenko and Abe⁶), M_p and m/p go to the correct reduced masses as X goes to infinity, and the dissociation energies obtained are correct using these hyper-spheroidal coordinates.

The eigenfunctions $\phi_n(\Omega; R)$ and eigenvalues $\epsilon_n(R)$ of the operator h for a fixed R are obtained by solving the Schroedinger equation

$$[h - \epsilon_n(R)] \phi_n(\Omega; R) = 0. \quad (17)$$

The total wavefunction ψ in the adiabatic approximation is then expressed by

$$\psi = R^{-5/2} \Phi_n(\Omega; R) \chi_n(R). \quad (18)$$

The radial wavefunction χ_n satisfies the following hyper-radial equation

$$\left[-\frac{1}{2M} \frac{d^2}{dR^2} + U_n(R) - E_v \right] \chi_n(R) = 0, \quad (19)$$

where

(20)

$$U_n(R) = \varepsilon_n(R) + \frac{15}{8MR^2} + W_{nn}(R),$$

and

$$W_{nn}(R) = -\frac{1}{2M} \left(\Phi_n, \frac{\partial^2}{\partial R^2} \Phi_n \right). \quad (21)$$

3. Results.

The following values of constants are used in this paper; $M_p = 1838.776$, $M_d = 3670.481$ and $1 \text{ Ry} = 13.6058 \text{ eV}$. For $J = 0$, we have calculated $\varepsilon_n(R)$ and $\Phi_n(\Omega; R)$ in Eq.(17) using a variational method. The form of the trial function adopted was

$$\Phi_n = \sqrt{\rho} \sum b_{in} \zeta_i(\xi, \eta; R), \quad (22)$$

where

$$\zeta_i(\xi, \eta; R) = \xi^{c_i} \exp(-\beta_i R \xi) P_{l_i}(\eta), \quad (23)$$

for $R \leq 10$ and

$$\zeta_i(\xi, \eta; R) = \xi^{c_i} \exp(-\beta_i R \xi) \eta^{l_i} \exp(-\gamma_i R \eta), \quad (24)$$

for $R \geq 10$. In Eq. (23), P_l denotes the Legendre polynomials. The b_{in} are the variational constants to be determined. Normalization of Φ_n is given by

$$(\Phi_n, \Phi_n) = \int \frac{1}{\rho^3} (\xi^2 - \eta^2) |\Phi_n|^2 d\xi d\eta d\varphi. \quad (25)$$

Using 77 basis functions, we have obtained $\varepsilon_n(R)$ and Φ_n for the lowest two states ($n = 1$ and 2) with $J = 0$, with good results for the region $R > 0.05$. Except around $R \approx 10$, less than 50 basis functions are needed to obtain good results for $\varepsilon_n(R)$. Our calculation reproduces the correct difference (3.7 meV) between the dissociation energies of the $n = 1$ and $n = 2$ states.

In Table 1, the hyper-radial adiabatic potential energies $\varepsilon_1(R)$ and diagonal non-adiabatic coupling term $W_{11}(R)$ are presented as a function of the hyper-radius R . It should be noted that W_{11} is proportional to $3/(4MR^2)$ at large R . This term cancels with a part of $\varepsilon_1(R)$ and $15/(8MR^2)$. Thus the asymptotic form of $U_1(R)$ is given by

$$U_1(R) \rightarrow \varepsilon_1(\infty) - \frac{2.254}{R^4}, \quad (26)$$

Therefore, without W_{11} , $U_1(R)$ does not give the correct asymptotic form for $\chi_1(R)$, although the dissociation energy $\varepsilon_1(\infty)$ is correct even without it. We have solved differential equation (19) numerically excluding and including W_{11} . The vibrational energies E_v obtained are given in Table 2. The results of the IA approximation²⁾, which also takes account of diagonal non-adiabatic terms, are given in the third column of this Table.

In addition we have also calculated E_v for $J = 0$ using the conventional adiabatic(CA) approximation, namely

$$\left[-\frac{1}{2M} \frac{d^2}{dX^2} + \frac{J(J+1)}{2MX^2} + (\Phi_n^{CA}, H \Phi_n^{CA}) - E_v^{CA} \right] \chi_n^{CA}(X) = 0, \quad (27)$$

where the adiabatic wavefunctions ϕ^{CA} are obtained from solving

$$\left[-\frac{1}{2m_e} \nabla_x^2 + V - \varepsilon_n^{CA}(X) \right] \Phi_n^{CA}(x, X) = 0. \quad (28)$$

The fourth column of Table 2 are the results of the CA approximation, Eq. (27), adjusted by using the full non-adiabatic corrections given by Wolniewicz and Poll⁸⁾. The hyper-spheroidal results with the diagonal non-adiabatic coupling and the IA results agree well with the CA results with the full non-adiabatic corrections. A comparison of the hyper-spheroidal results with the IA results shows that the hyper-spheroidal results are in better agreement with the CA results. On the other hand, the hyper-spheroidal results, without including W_{11} , are consistently higher than the other three results. Therefore even in the hyper-spheroidal approach, the diagonal non-adiabatic effects must be taken into account to attain accurate values for E_v . This is because not only the correct dissociation limit but also the correct asymptotic form of $\varepsilon_1(R)$ is necessary to obtain reliable values for E_v . Macek and Jerjian³⁾ did not properly take into account of the correct asymptotic form of $\varepsilon_1(R)$. They omitted these parts of the Coulomb interaction V which were of the order m_e/M_p , but they kept the terms that lead to the correct dissociation limit. They also excluded the diagonal non-adiabatic interactions. Thus they did not use the correct asymptotic form for $\varepsilon_1(R)$. Despite their approximations, they claim that their results are close to those of Wolniewicz and Poll⁸⁾, who have included non-adiabatic, relativistic and radiative corrections. There is a possibility that the terms neglected by Macek and Jerjian cancel each other and this fortuitous cancellation produces good results. Therefore we have solved Eq. (23) of their paper³⁾ neglecting the

same terms as they did in an effort to reproduce their results. In our calculation, the adiabatic potential curve was computed by the method proposed by Bates and Carson⁹⁾. However, we have not been able to reproduce their results. To check our computer programme, we have also repeated the calculation in the "Standard Adiabatic"(SA) approximation. The results were identical with those of Struensee et al.²⁾ differing only by 0.01cm^{-1} for a few vibrational levels.

For $J \neq 0$, the rotational energy term contributes little to the total energy. Since the Coriolis interaction $\hat{J} \cdot \hat{l}$ is off-diagonal for Σ states and since $\rho \approx 1$ for HD^+ , we neglect $\hat{J} \cdot \hat{l}$ and take $\rho = 1$ in the rotational energy. Thus the adiabatic Hamiltonian, Eq. (10), for $J \neq 0$ can be well approximated by

$$h = -\frac{\rho^2}{2m} \nabla_r^2 + \frac{\hat{J}^2}{2MR^2} + V + \frac{\rho \hat{q}}{MR^2}. \quad (10')$$

Therefore, the rotational-vibrational energies for $J \neq 0$ can be obtained by adding the centrifugal potential $J(J+1)/(2MR^2)$ to $U_1(R)$ in Eqs. (19) and (20). Errors are of order m/M for the rotational energy. This is an additional approximation. It is possible, if necessary, to treat the angular momentum term accurately just as it has been done in the muonic molecules with $J \neq 0$ ¹⁰⁾. The results are given in Table 3 and compared with the CA results, Eq. (27), adjusted by using the full non-adiabatic correction given by Wolniewicz and Poll⁷⁾. Agreement between the two results is very satisfactory.

In conclusion, we have obtained good results for both $J = 0$ and $J \neq 0$ rotational-vibrational energies of HD^+ using the hyper-spheroidal coordinates.

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Figure caption

Fig. 1. Coordinates for the HD⁺ molecular ion.

Fig. 1

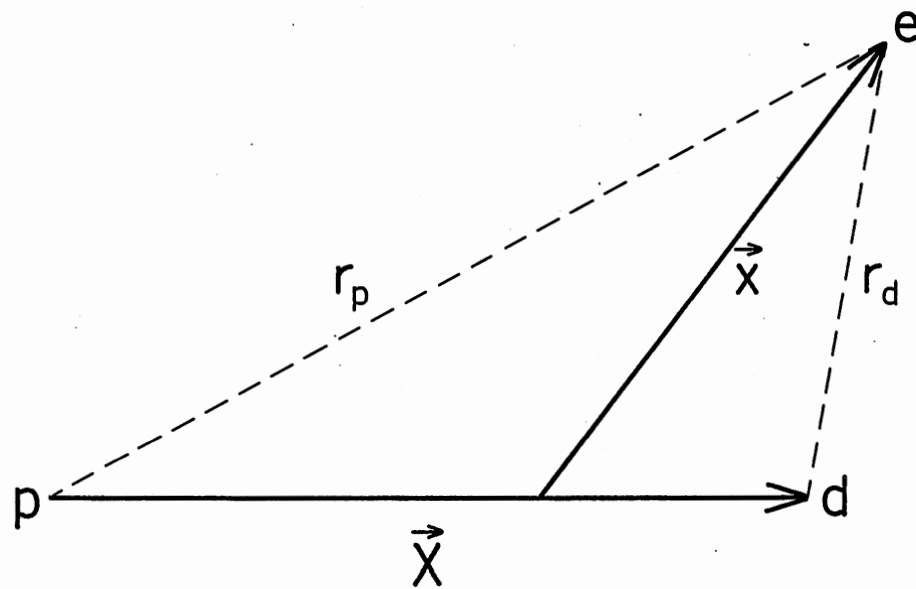


Table 1. Hyper-radial adiabatic potential energy ε_1 and the diagonal non-adiabatic correction term W_{11} as a function of hyper-radius R in units of $e = \hbar = m = 1$, where m is defined in Eq. (4).

Numbers in parentheses are powers of 10.

R	$\varepsilon_1(R)$	$W_{11}(R)$
0.1	8.6139359	0.183(-1)
0.5	0.7607416	0.881(-3)
1.0	0.0468609	0.170(-3)
1.2	-0.0299498	0.109(-3)
1.4	-0.0707197	0.759(-4)
1.6	-0.0915123	0.556(-4)
1.8	-0.1007148	0.427(-4)
2.0	-0.1030117	0.341(-4)
2.2	-0.1011536	0.281(-4)
2.4	-0.0968181	0.239(-4)
2.6	-0.0910580	0.208(-4)
2.8	-0.0845485	0.186(-4)
3.0	-0.0777285	0.169(-4)
4.0	-0.0461632	0.130(-4)
5.0	-0.0244494	0.114(-4)
6.0	-0.0119670	0.947(-5)
7.0	-0.0055722	0.734(-5)
8.0	-0.0025365	0.559(-5)
9.0	-0.0011550	0.471(-5)
10.0	-0.0005369	0.630(-5)
15.0	-0.0000538	0.159(-5)
20.0	-0.0000188	0.766(-6)

Table 2. The dissociation energies E_v of HD^+ ($J=0$) relative to the 1S state of the D atom in cm^{-1} .

v	1) H. R.	2) H. R.	3) I. A.	4) C. A.
0	21523.3	21515.9	21515.92	21516.02
1	19610.0	19602.8	19602.80	19603.05
2	17792.8	17785.9	17785.82	17786.21
3	16068.9	16062.2	16062.12	16062.64
4	14435.8	14429.3	14429.22	14429.86
5	12891.4	12885.2	12885.00	12885.74
6	11433.9	11427.9	11427.68	11428.52
7	10062.1	10056.1	10055.88	10056.80
8	8774.5	8768.8	8768.53	8769.52
9	7570.7	7565.3	7564.96	7566.01
10	6450.4	6445.2	6444.85	6445.94
11	5413.7	5408.7	5408.30	5409.42
12	4461.0	4456.2	4455.82	4456.96
13	3593.3	3588.8	3588.36	3589.50
14	2812.0	2807.8	2807.39	2808.49
15	2119.2	2115.3	2114.87	2115.93
16	1517.4	1513.8	1513.42	1514.41
17	1009.8	1006.7	1006.28	1007.16
18	600.5	597.8	597.43	598.17
19	294.0	291.8	291.55	292.11
20	95.6	93.6	93.55	93.64
21	11.2	9.1	8.76	

1) Results obtained by using the hyper-radial adiabatic potential without the diagonal non-adiabatic correction.

2) Results obtained by using the hyper-radial adiabatic potential with the diagonal non-adiabatic correction.

3) (IA) results of Struensee, Cohen and Pack²⁾.

4) (CA) results with the full non-adiabatic correction given by Wolniewicz and Poll⁸⁾.

Table 3. The dissociation energies of HD^+ relative to the 1S state of the D atom in cm^{-1} .

v	J=1		J=2		J=3	
	1)	2)				
	H. R.	C. A.	H. R.	C. A.	H. R.	C. A.
0	21472.1	21472.16	21384.7	21384.71	21254.2	21254.18
1	19561.0	19561.19	19477.6	19477.73	19353.1	19353.17
2	17746.0	17746.29	17666.4	17666.71	17547.7	17547.94
3	16024.2	16024.62	15948.4	15948.80	15835.3	15835.65
4	14393.2	14393.68	14321.1	14321.54	14213.5	14213.89
5	12850.8	12851.36	12782.3	12782.82	12680.1	12680.55
6	11395.3	11395.92	11330.3	11330.91	11233.4	11233.93
7	10025.3	10025.94	9963.8	9964.43	9872.1	9872.67
8	8739.7	8740.40	8681.7	8682.34	8595.1	8595.76
9	7537.9	7538.60	7483.3	7484.00	7401.9	7402.57
10	6419.5	6420.27	6368.4	6369.11	6292.2	6292.84
11	5384.8	5385.49	5337.1	5337.80	5266.1	5266.73
12	4434.1	4434.78	4389.9	4390.61	4324.1	4324.80
13	3568.4	3569.11	3527.8	3528.53	3467.4	3468.08
14	2789.3	2789.95	2752.4	2753.05	2697.5	2698.12
15	2098.7	2099.30	2065.6	2066.20	2016.4	2016.99
16	1499.2	1499.76	1470.1	1470.65	1426.9	1427.43
17	994.1	994.62	969.3	969.73	932.4	932.84
18	587.5	587.89	567.1	567.52	537.0	537.43
19	284.0	284.28	268.6	268.84	245.9	246.17
20	88.5	88.53	78.6	78.55	64.2	64.18
21	7.5		4.6		1.2	

1) Results obtained using the hyper-radial adiabatic potential with the diagonal non-adiabatic correction.

2) (CA) results with the full non-adiabatic correction given by Wolniewicz and Poll⁸⁾.