

# Static properties and the Stark effect of the ground state of the HD molecular ion

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We have calculated the static properties of the ground state of the HD<sup>+</sup> ion and its lowest-lying P state without making use of the Born-Oppenheimer approximation, as was done in the case of H<sub>2</sub><sup>+</sup> and D<sub>2</sub><sup>+</sup> [1]. The ion is treated as a three-body system whose ground state is spherically symmetric. The wave function is of generalized Hylleraas type, but it is necessary to include high powers of internuclear distance to localize the nuclear motion. We obtain E<sub>0</sub>=-1.195 795 889 for 560 terms and E<sub>p</sub>=-1.195 371 602 Ry for 728 terms compared to E<sub>0</sub>=-1.195 795 931 and E<sub>p</sub>=-1.195 396 256 Ry of earlier calculations [2]. Expectation values are obtained of various operators, the Fermi contact parameters, and the permanent quadrupole moment. The cusp conditions are also calculated. These results are compared with those obtained by Bishop and Cheung [3]. The polarizability is then calculated using second-order perturbation theory with intermediate P pseudostates [4]. Since the nuclei in HD<sup>+</sup> are not of equal mass there is a dipole coupling between the lowest two rotational states, which are almost degenerate. The polarizability is given by

$$\alpha_1 = \sum_p \frac{\langle 0|d|p \rangle \langle p|d|0 \rangle}{E_p - E_0} a_0^3 \quad (1)$$

where d is the dipole operator and 0 and p refer to the ground and P states. The dipole operator d is given by

$$d = 2 \left[ \frac{M_D + 1}{M_T} \vec{r}_1 + \frac{M_P + 1}{M_T} \vec{r}_2 \right] \cdot \hat{e} \quad (2)$$

M<sub>P</sub> and M<sub>D</sub> are the masses of proton and deuteron, respectively and r<sub>1</sub> and r<sub>2</sub> are the distances of the proton and deuteron from the electron. Also

$$M_T = M_P + M_D + 1 \quad (3)$$

Using the ground state wave function obtained with 560 terms we calculate α<sub>1</sub> as the number of P pseudostates is varied. We find that almost all of the calculated polarizability comes from the lowest P-state in the intermediate sum in Eq. (1). The polarizability due to this single term is then α = 392.0814a<sub>0</sub><sup>3</sup>, and the sum over all the remaining intermediate states contributes α<sub>s</sub> = 3.2076a<sub>0</sub><sup>3</sup>. The total polarizability is 395.289a<sub>0</sub><sup>3</sup> which is very much larger than might be expected from the results [4] in H<sub>2</sub><sup>+</sup> and D<sub>2</sub><sup>+</sup>. This can be traced to the fact that

HD<sup>+</sup> is heteronuclear, and so there is coupling between the ground state and the low-lying P state, which would not happen in the homonuclear case. Also the perturbation formula (1) is valid only if the perturbation is small compared to the spacing of the unperturbed energy levels. Unlike the homonuclear case this condition is not satisfied in HD<sup>+</sup>. The calculated polarizability is meaningful only in very weak electric fields, much weaker than in those found in the Rydberg states of HD. To correct this and to calculate the Stark shift realistically we go to a variational method. We must include at least the two lowest opposite-parity states and as many of the higher ones as possible to obtain a more reasonable form of the polarization energy of the system. At high fields (or short distances) this energy goes like  $R^{-2}$  and for weak fields it goes like  $R^{-4}$ . As an estimate of the effect of the polarizability on the Rydberg energy levels of the HD molecule we compute the expectation value of the potential excluding the lowest P-state:

$$\Delta_{NL} = -\alpha_s \int \Psi_{NL}(R) \frac{1}{R^4} \Psi_{NL}(R) d^3 R \quad (4)$$

where  $\Psi$  is a hydrogenic wave function, and we show the results in Table 1.

When combined with relativistic corrections and higher-order terms these energy shifts may not be unrealistic for application to the problem of Rydberg states of HD [5].

Table 1: Energy shift  $\Delta_{NL}$  of a series of Rydberg levels due to the polarizability of the HD<sup>+</sup> ionic core omitting the lowest rotationally excited level in the summation over the intermediate states.

N	L	$-\Delta_{NL}$ (MHz)
5	4	53600
6	4	34466
	5	10966
7	4	23013
	5	7610.6
	6	2927.1
8	4	15986
	5	5404.9
	6	2144.8
	7	720.08
9	4	11501
	5	3943.6
	6	1594.9
	7	720.08
	8	350.41
10	4	8527.4
	5	2951.8
	6	1208.8
	7	554.8
	8	275.89
	9	145.2

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