

Breakdown of the Born-Oppenheimer Approximation in the Calculation of Electric Hyperpolarizabilities

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For the first time a nonadiabatic (all-particle) calculation has been carried out for the electric polarizabilities and hyperpolarizabilities of H_2^+ , HD^+ , and D_2^+ in their lowest rovibronic states. The value of the hyperpolarizability γ is dramatically different from that which would be assumed from calculations based on the Born-Oppenheimer approximation unless account is taken of a vibrational contribution which (unlike its counterpart for the α polarizability) is nonzero even for a homonuclear diatomic molecule. For H_2^+ we find that $\alpha_{zz} = 5.827$ a.u. and $\gamma_{zzzz} = 2.2 \times 10^3$ a.u.

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Normally the effect of using the Born-Oppenheimer approximation, as opposed to an all-particle (nuclei and electrons) calculation (the nonadiabatic method), for the calculation of molecular properties is minimal and only of interest for making comparisons with highly accurate spectroscopic measurements. Exceptions to this rule are, of course, properties, such as the dipole moment of HD^+ , which are purely non-Born-Oppenheimer in origin and can only be determined by a nonadiabatic calculation which puts all particles on an equal footing. In this Letter we report a calculation on H_2^+ , HD^+ , and D_2^+ of the dipole polarizability α_{zz} and the hyperpolarizability γ_{zzzz} , where we have found that the nonadiabatic value of γ_{zzzz} is startlingly different from what would be assumed on the basis of a Born-Oppenheimer (adiabatic) calculation if certain vibrational contributions are neglected. In the light of recent experimental advances in the determination of molecular hyperpolarizabilities,¹ this discovery has important implications.

Electric polarizabilities may be defined by an expansion of the energy or dipole moment of a molecule in the presence of a uniform finite field F . In this work we place the field along the nuclear axis (z) and have the following simple expressions²:

$$E(F_z) = E_0 - \mu_z^0 F_z - \frac{1}{2} \alpha_{zz} F_z^2 - \frac{1}{6} \beta_{zzz} F_z^3 - \frac{1}{24} \gamma_{zzzz} F_z^4 + \dots, \quad (1)$$

$$\mu_z(F_z) = \mu_z^0 + \alpha_{zz} F_z + \frac{1}{2} \beta_{zzz} F_z^2 + \frac{1}{6} \gamma_{zzzz} F_z^3 + \dots \quad (2)$$

We have calculated $E(F_z)$ and $\mu_z(F_z)$ with $F_z = 0, 0.001, 0.0025, 0.005, 0.0075,$ and 0.01 a.u. for H_2^+ and D_2^+ and $F_z = 0, \pm 0.001, \pm 0.0025,$ and ± 0.005 a.u. for HD^+ . These calculations were performed variationally with wave functions of the form³

$$\Psi = \sum_{i=0}^9 \sum_{j=0}^{14} \sum_{k=0}^{15} c_{ijk} \phi_{ijk}, \quad (3)$$

with basis functions ϕ_{ijk} excluded if $i + j + k > 17$ and j is even and if $i + j + k > 15$ and j is odd: This leads to an 888-term function with 888 linear coefficients c_{ijk} . Such a basis set allows the energy to have converged in the eleventh significant digit. The ϕ_{ijk} are defined by

$$\phi_{ijk}(\xi, \eta, R) = \exp(-\alpha\xi) \cosh(\beta\eta) \times \xi^i \eta^j R^{-3/2} \exp(-x^2/2) H_k(x), \quad (4)$$

where ξ and η are the usual elliptical coordinates of the electron, R is the internuclear distance, $x = \gamma(R - \delta)$, and $H_k(x)$ are the Hermite polynomials. The nonlinear parameters used were³ $\alpha = 1.6$, $\beta = 0.75$, $\delta = 2.1$ (all ions), and $\gamma = 3.0$ (H_2^+), 3.25 (HD^+), and 3.6 (D_2^+). Only the lowest rovibronic state was investigated. Atomic units were used throughout: energy = 4.3598×10^{-18} J, dipole moment = 8.4784×10^{-30} C m, $\alpha = 0.16488 \times 10^{-40}$ C² m² J⁻¹, $\beta = 0.32063 \times 10^{-52}$ C³ m³ J⁻², $\gamma = 0.62360 \times 10^{-64}$ C⁴ m⁴ J⁻³. The total Hamiltonian, used in nonadiabatic calculations, involves the masses of the nuclei and we have taken $m_e/m_p = 0.000544617$ (Van Dyck and Schwinberg⁴) and $m_e/m_d = 0.000272444$. For the properties of HD^+ it is necessary to specify that the z coordinate is in the direction H^+ to D^+ and that the origin is at the geometric center of the nuclei.

Our major results are presented in Table I and are the outcome of a number of accuracy tests: (a) the final large basis set (888 terms) was chosen after much investigation and allows, as we have said, energy convergence to be achieved on the eleventh significant digit. (b) Some calculations were made in quadruple precision to detect any machine inaccuracy; none was found. (c) Fairly small fields were used so that, when $E(F_z)$ and $\mu_z(F_z)$ are fitted to Eqs. (1) and (2) in truncated form, discarded terms are negligible. Small fields also ensure that what is, in principle, an unbounded problem, is for all practical purposes then bounded. (d) As a measure of accuracy several different polynomials in F_z were used for fitting. Four

TABLE I. Properties of H_2^+ , HD^+ , and D_2^+ in atomic units.

Species	Method	E_0	μ_z^0	α_{zz}	β_{zzz}	γ_{zzzz}
H_2^+	Eq. (1), series A ^a	-0.597 139 063 18	$\sim 10^{-7e}$	5.8274	$\sim 10^{-2e}$	2.27×10^3
	series B ^b	-0.597 139 063 16	...	5.8272	...	2.19×10^3
	Eq. (2), series C ^c	5.8272	$\sim 10^{-2e}$	2.14×10^3
	series D ^d	5.8272	...	2.19×10^3
HD^+	Eq. (1), series A ^a	-0.597 897 967 80	5.7644×10^{-4}	5.7170	0.0850	2.08×10^3
	Eq. (2), series C ^c	...	5.7644×10^{-4}	5.7170	0.0851	2.08×10^3
D_2^+	Eq. (1), series A ^a	-0.598 788 782 22	$\sim 10^{-7e}$	5.5894	$\sim 10^{-2e}$	2.01×10^3
	series B ^b	-0.598 788 782 21	...	5.5892	...	1.95×10^3
	Eq. (2), series C ^c	5.5892	$\sim 10^{-2e}$	1.91×10^3
	series D ^d	5.5892	...	1.95×10^3

^aEven and odd powers of F_z up to F_z^4 fitted to $E(F_z)$.

^bEven powers of F_z up to F_z^6 fitted to $E(F_z)$.

^cEven and odd powers of F_z up to F_z^3 fitted to $\mu_z(F_z)/F_z$ for H_2^+ and D_2^+ and to $\mu_z(F_z)$ for HD^+ .

^dEven powers of F_z up to F_z^4 fitted to $\mu_z(F_z)/F_z$.

^eA measure of fitting accuracy only.

examples are shown in Table I: using for $E(F_z)$ (A) even and odd powers of F_z up to F_z^4 or (B) only even powers up to F_z^6 ; using for $\mu_z(F_z)/F_z$ (C) even and odd powers of F_z up to F_z^3 or (D) only even powers up to F_z^4 . For H_2^+ and D_2^+ μ_z and β_{zzz} should be, by symmetry, identically zero and the small values found with use of series A and C validate our results. (e) A final measure of the reliability of the results is that those found by either Eq. (1) or Eq. (2) are essentially the same. All the field strengths mentioned previously were used in the fitting except the $\mu_z(0)$ value (0) for H_2^+ and D_2^+ .

The values of E_0 , the lowest (ground-state) energy, in Table I are slightly lower, because of the larger basis set, than the previous best values given by Bishop and Cheung.³ The value of μ_z^0 for HD^+ , 5.7644×10^{-4} a.u., in the sense H^+ to D^+ , is in good agreement with the nonadiabatic value of 5.7648×10^{-4} a.u. of Bishop and Cheung.⁵ The nonadiabatic values of α_{zz} for H_2^+ may be compared with earlier adiabatic calculations: For a fixed internuclear separation (R) of 2.0 a.u. the value is⁶ 5.077 65 a.u.; when values for several R are averaged over the adiabatic ground-vibrational wave function it is⁷ 5.8431 a.u.; a sum-over-states value found by the method of Bishop and Cheung⁸ is 5.834 a.u. for the rovibronic ground state.⁹ The small difference between the last two values is in line with the discussion in Bishop, Cheung, and Buckingham¹⁰; the nonadiabatic value 5.8274 a.u. is slightly lower than the adiabatic value. The decrease in α_{zz} in going from H_2^+ to HD^+ to D_2^+ is in line with the decrease in the expectation value⁵ of z^2 : It is generally assumed that a less diffuse electronic distribution leads to a lower polarizability.

The value of β for HD^+ , 0.0850 a.u., an intrinsically nonadiabatic property has not been previously deter-

mined.

The most interesting result we have found is that γ_{zzzz} for H_2^+ is approximately 2.2×10^3 a.u. This is about 10 times bigger than and of opposite sign to the adiabatic value (-194 a.u.).⁷ The value for a fixed R of 2.0 a.u. is¹¹ -40.935 a.u. When the basis functions in Eq. (3) are restricted to $k=0$ (i.e., only one type of component in R) then negative values of γ_{zzzz} are achieved—hence the difference between the values just cited is a result of vibronic coupling and it is clear that hyperpolarizabilities are extremely sensitive to this phenomenon. Another way of putting this is that there is a large purely vibrational contribution that must be added to the adiabatic result. An approximate formula for this term,¹² found along the lines of Pandey and Santry,¹³ is

$$\gamma_{zzzz}(\text{vib}) = (3/m\omega^2)(\partial\alpha/\partial R)^2,$$

where m is the reduced nuclear mass, ω is the fundamental vibrational frequency and $\partial\alpha/\partial R$ is the derivative of the dipole polarizability α with respect to the internuclear distance (evaluated near the equilibrium). For H_2^+ , $\gamma_{zzzz}(\text{vib}) \approx 2020$ a.u. and approximately accounts for most of the dramatic change we have

TABLE II. Expectation values (in atomic units) of R for different fields (F_z) along the nuclear axis.

F_z	H_2^+	HD^+	D_2^+
0	2.063 91	2.054 80	2.044 07
0.0025	2.064 20	2.055 09	2.044 33
0.005	2.065 05	2.055 92	2.045 12
0.01	2.068 50	...	2.048 31

found.

Finally, in Table II, we give expectation values of the internuclear separation as a function of field strength. The small increase in separation with field strength is compatible with a similar investigation on HF by Adamowicz and Bartlett.¹⁴ For H_2^+ , \bar{R} may be expressed as

$$\bar{R} = 2.0639 + 45.8F^2$$

for HD^+ (making use of values of \bar{R} with negative as well as positive fields) as

$$\bar{R} = 2.0548 + 4.89 \times 10^{-3}F + 43.9F^2$$

and for D_2^+ as

$$\bar{R} = 2.0441 + 42.4F^2.$$

Using the Born-Oppenheimer approximation and making a Taylor-series expansion¹⁵ the coefficient of F^2 is approximately given by

$$(\partial\alpha/\partial R)_{Re}/2k$$

where k is the force constant. We have calculated $(\partial\alpha/\partial R)$ at $R = 2.06a_0$ from a series of Born-Oppenheimer results for α to be 7.85 and, since k is equal to 0.103,¹⁶ the coefficient by this formula would be 38.1, which is in reasonable agreement with the exact values given above.

Full details of these calculations, together with an adiabatic investigation of the unbounded nature of the problem, which is particularly germane for electronically excited states, will be published later.

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