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Physical origins of high-order nonadiabatic molecular electric polarizabilities: Application to a twentieth-order perturbation study of $H_2{}^+$

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It is demonstrated theoretically for arbitrary diatomic molecules (and atoms) and verified numerically with a twentieth-order perturbation study of the Stark effect for the ground state of $H_2{}^+$ that high-order nonadiabatic electric polarizabilities in each order result from the delicate partial balancing of larger opposing perturbational shifts in their kinetic, nuclear-potential, and field-potential components, where the relative magnitudes and signs of these component shifts can be precisely determined by general *a priori* relationships. This method of analysis, based upon a combination of the Stark virial, Hellmann-Feynman, and remainder theorems, and implemented via the perturbational-variational Rayleigh-Ritz formalism, provides a novel mechanism for studying in detail the physical origins of molecular polarizabilities.

Quite recently, large-order perturbation theory[1] (LOPT) was applied[2,3] for the first time to the study of the Stark effect for the hydrogen molecular ion $H_2{}^+$; in these studies, LOPT was implemented via the powerful and flexible perturbational-variational Rayleigh-Ritz (PV-RR) matrix formalism.[4] To obtain results of highest acccuracy directly without the requirement of making supplementary vibrational corrections, the initial LOPT PV-RR Stark calculations for $H_2{}^+$ were performed[2] *nonadiabatically*,[5] i.e., without invoking the customary Born-Oppenheimer approximation but, rather, treating $H_2{}^+$ as a three-particle system with all particles on an equal footing. Subsequently, as a sensitive test of the influence of nuclear motion on polarizabilities in higher order, the LOPT PV-RR calculations were repeated[3] *adiabatically*, i.e., within the Born-Oppenheimer (clamped-nuclei) approximation and without any correction for nuclear motion. These studies yielded the nonadiabatic and adiabatic exact Rayleigh-Schrödinger (RS) ground-state polarizability (eigenvalue) series through twentieth and thirtieth order, respectively; earlier Stark expansions for $H_2{}^+$ were limited to fourth order.[6] These high-order polarizability series for $H_2{}^+$, as well as those previously derived for hydrogenic ions,[7-9] are of considerable interest for a number of reasons.[1-3,7-10]

In general, the polarizabilities are a measure of the ease with which the molecular charge distribution can be distorted in the presence of a uniform electric field. Little or nothing is known quantitatively, however, concerning the interplay of the various, possibly competing, physical factors which lead to the molecular polarizabilities. In the present work, we investigate these physical origins in detail for the first time by resolving the high-order nonadiabatic polarizabilities for $H_2{}^+$ into their kinetic- and potential-energy components, where the latter are further decomposed into their nuclear- and field-potential components; aside from a recent preliminary application[9] of the procedure to hydrogenic ions, we are not aware of any similar calculations in the literature for either atoms or molecules, not even low-order ones. As we shall demonstrate theoretically *for arbitrary diatomic molecules (and atoms)*, and verify numerically for $H_2{}^+$, the total nonadiabatic polarizabilities in each order result from the delicate partial balancing of larger opposing perturbational shifts in their energetic components, where the relative magnitudes and signs of these shifts can be precisely determined by general *a priori* relationships. In particular, we report here the RS ground-state series of all three nonadiabatic energetic components for $H_2{}^+$ through twentieth order. These were obtained within the framework of the PV-RR formalism by using two different independent methods.

In the center-of-mass system, the perturbed nonadiabatic Hamiltonian operator $\hat{H}$ for $H_2{}^+$, in a uniform electrostatic field F_z parallel to the internuclear (z) axis, has the form[5]

$$\hat{H} = \hat{H}(F_z) = \hat{H}_0 + \hat{H}_1 F_z \; , \tag{1}$$

where the unperturbed (field free) $\hat{H}_0$, and the kinetic and nuclear-potential operators, $\hat{T}$ and $\hat{V}_0$, respectively, are given by[11]

$$\hat{H}_0 = \hat{T} + \hat{V}_0 \; , \tag{2}$$

$$\hat{T} = -\tfrac{1}{2}(1+\tfrac{1}{4}\mu^{-1})\nabla_e^2 - \tfrac{1}{2}\mu^{-1}\nabla_R^2 \; , \tag{3a}$$

$$\hat{V}_0 = -r_A^{-1} - r_B^{-1} + R^{-1} \; , \tag{3b}$$

and the perturbing field-potential operator $\hat{H}_1$ can be written as[2,5,6]

$$\hat{H}_1 = fz \; , \tag{4a}$$

$$f = 1 + m_e/M \approx 1.000\,272\,234 \; . \tag{4b}$$

Here, ∇_e^2 and ∇_R^2 are, respectively, the Laplacian operator for the electron relative to the geometric center of the nuclei A and B, and for one nucleus relative to the other, μ is the reduced nuclear mass; r_A and r_B have their usual significance, R is the internuclear separation (which in the nonadiabatic approach is treated as a variable of integration), z is the electronic coordinate relative to the geometric center of the nuclei; m_e and M are, respectively, the mass of the electron and the total molecular mass, and the numerical factor[12] f stems from the nonadiabatic treatment. We seek the RS series in powers of F_z for the perturbed normalized eigenfunctions $|\psi^2(F_z)\rangle$ and eigenvalues $E^s(F_z)$ from which we then obtain the corresponding RS series of the energetic components $\langle\hat{T}\rangle^s(F_z)$, $\langle\hat{V}_0\rangle^s(F_z)$, and $\langle\hat{H}_1\rangle^s(F_z)$; here, the superscript s labels the state and $\langle\hat{A}\rangle^s(F_z)$ denotes the expectation value $\langle\psi^s(F_z)|\hat{A}|\psi^s(F_z)\rangle$ of an arbitrary operator $\hat{A}$ independent of F_z. To initiate the PV-RR procedure, introduce the highly accurate nonadiabatic Rayleigh-Ritz ansatz[11] used in the previous PV-RR calculations[2] of high-order nonadiabatic polarizabilities. One then forms the nonadiabatic matrix eigenvalue equation

$$\mathbf{H}\mathbf{C}^s = E^s\mathbf{S}\mathbf{C}^s \ , \tag{5}$$

where $\mathbf{H}$ and $\mathbf{S}$ are, respectively, the total perturbed Hamiltonian and overlap matrices and $\mathbf{C}^s$ is the column eigenvector composed of the linear variational coefficients. In contrast, however, to the conventional Rayleigh-Ritz procedure with its attendant problem of variational collapse,[13] $\mathbf{H}$ is partitioned according to (1) as

$$\mathbf{H} = \mathbf{H}(F_z) = \mathbf{H}_0 + \mathbf{H}_1 F_z \ , \tag{6}$$

where F_z is not assigned fixed numerical values but, rather, treated as a variable perturbing parameter. Application of the PV-RR formalism to (5) and (6) then yields the series

$$\mathbf{C}^s = \mathbf{C}^s(F_z) = \sum_{j=0}^{\infty} \mathbf{C}_j^s F_z^j \ , \tag{7a}$$

$$E^s = E^s(F_z) = \sum_{j=0}^{\infty} E_j^s F_z^j \ , \tag{7b}$$

$$\langle\hat{A}\rangle^s = \langle\hat{A}\rangle^s(F_z) = \sum_{j=0}^{\infty} \langle\hat{A}\rangle_j^s F_z^j, \ \hat{A} = \hat{T},\hat{V}_0,\hat{H}_1 \tag{7c}$$

to high order for the states of interest in a single computer run. The extent to which the PV-RR eigenvalue series (7b) agrees with the corresponding exact RS series depends upon the effective choice and degree of saturation of the basis set, and can be determined[2,3,9] by examining the variational convergence of the individual E_j^s; as we shall demonstrate, similar remarks apply to the expectation-value series (7c). To maintain close connection with the widely used notation[14] for molecular polarizability studies, we write the E_j^s of (7b) as

$$E_j^s = -\alpha_j^s/j!, \ j = 1,2,\ldots, \tag{8}$$

and refer to the α_j^s collectively as polarizabilities. It follows from (1), (2), and (8) that, in general, one can express the α_j^s as the sum of the energetic components

$$\alpha_j^s = \alpha_j^{K,s} + \alpha_j^{N,s} + \alpha_j^{F,s} \ , \tag{9}$$

where the kinetic, nuclear-potential, and field-potential components, $\alpha_j^{K,s}$, $\alpha_j^{N,s}$, and $\alpha_j^{F,s}$, respectively, are defined as

$$\alpha_j^{K,s} \equiv -j!\langle\hat{T}\rangle_j^s \ , \tag{10a}$$

$$\alpha_j^{N,s} \equiv -j!\langle\hat{V}_0\rangle_j^s \ , \tag{10b}$$

$$\alpha_j^{F,s} \equiv -j!\langle\hat{H}_1\rangle_{j-1}^s \ . \tag{10c}$$

As previously mentioned, the components (10) are determined by two independent methods: (1) From the basic PV-RR formalism,[4] we have the purely numerical procedure,

$$\langle\hat{A}\rangle_j^s = \sum_{k=0}^{j} (\mathbf{C}_k^s)^\dagger \mathbf{A}\mathbf{C}_{j-k}^s, \ \mathbf{A} = \mathbf{T},\mathbf{V}_0,\mathbf{H}_1 \ , \tag{11}$$

which, together with (10), yields the components directly; here $\mathbf{A}$ is the matrix representation $\hat{A}$ in the chosen basis. (2) We also have at our disposal, however, the Stark *nonadiabatic* virial theorem,[15]

$$2\alpha_j^{K,s} + \alpha_j^{N,s} - \alpha_j^{F,s} = 0 \ , \tag{12}$$

and the Hellmann-Feynman theorem,[4,16]

$$\alpha_j^{F,s} = j\alpha_j^s \ . \tag{13}$$

On combining (9), (12), and (13), one obtains

$$\alpha_j^{K,s} = (2j-1)\alpha_j^s \ , \tag{14a}$$

$$\alpha_j^{N,s} = (2-3j)\alpha_j^s \ . \tag{14b}$$

Thus, (13) and (14) completely separate the components and enable their indirect theoretical determination via the α_j^s.

Note that if (11) is used, a knowledge of the eigenvector series (7a) through nth order only suffices to compute the component series (7c) through like order; on the other hand, with (13) and (14), the component series can be extended through $(2n+1)$th order, with but negligible computational effort, from the nth-order eigenvector series since the latter yields the polarizability series (7b) through $(2n+1)$th order via the PV-RR remainder theorem.[4] This distinction between the two approaches leads to a number of additional interesting consequences.[17] Equations (13) and (14), which hold for the exact RS nonadiabatic polarizabilities of all states of all diatomic molecules (and atoms), are the principal theoretical findings of this work, and display quantitatively the previously mentioned delicate partial balancing of the components: In particular, note that for $j \geq 2$, $|\alpha_j^{N,s}| > |\alpha_j^{K,s}| > |\alpha_j^{F,s}| > |\alpha_j^s|$, and for all j, α_j^s, $\alpha_j^{K,s}$, and $\alpha_j^{F,s}$ are of like sign, while $\alpha_j^{N,s}$ is of the opposite sign; thus, for $j = 1,2,\ldots$, we can write

$$|\alpha_j^s| = \left| \, |\alpha_j^{K,s} + \alpha_j^{F,s}| - |\alpha_j^{N,s}| \, \right| \ . \tag{15}$$

Further, if the Bender-Wu[1,10,18]-type asymptotic formulas for the large-order α_j^s should be determined, (13) and (14) would then immediately yield the corresponding asymptotic formulas for the components, as has been recently demonstrated[9] for hydrogenic ions.

For a homopolar molecule such as $H_2{}^+$ in a uniform electric field parallel to the internuclear axis, the odd order α_j^s and their components all vanish identically due to symmetry. As a test of our formalism, however, we shall not impose this constraint explicitly, but numerically evaluate

TABLE I. Comparison of variational convergence as a function[a] of N of PV-RR nonadiabatic polarizability components α_2^K, α_2^N, and α_2^F (in atomic units).

N	α_2^K	α_2^N	α_2^F
44	16.8	−22.7	11.708
	17.563	−23.417	11.708
68	17.21	−23.04	11.674
	17.512	−23.349	11.674
100	17.427	−23.260	11.6659
	17.4988	−23.3318	11.6659
140	17.469	−23.330	11.6622
	17.4933	−23.3324	11.6622
190	17.4821	−23.3127	11.66147
	17.49172	−23.32229	11.66147
250	17.4889	−23.3194	11.66086
	17.49129	−23.32172	11.66086
320	17.4902	−23.3206	11.66076
	17.49114	−23.32152	11.66076
400	17.49072	−23.32108	11.660723
	17.491084	−23.321446	11.660723
490	17.49096	−23.32132	11.660714
	17.491071	−23.321427	11.660714
540	17.49099	−23.32135	11.660712
	17.491068	−23.321424	11.660712

[a] For each value of N, the first row of entries is computed with Eq. (11) and the second with Eqs. (13) and (14).

all coefficients. To illustrate our theory, we apply the procedure to the ground state of H_2^+ and, for brevity, suppress the state superscript. All calculations were performed in ordinary double-precision arithmetic (about 16 significant digits) with an efficient computer program for implementing PV-RR, which incorporates the basic PV-RR algorithms[4] augmented by the above-cited theorems. The computational details are precisely as described in Ref. 2, both in fixing the nonlinear parameters and in systematically constructing a sequence of variational eigenfunctions with the number of basis functions N increasing over the range of $N = 2, 6, 14, \ldots, 400, 490, 540$. In all calculations, the odd-order coefficients were found to vanish identically as required. In Table I are collected our nonadiabatic values of α_2^K, α_2^N, and α_2^F as functions of N, computed both with (11) and with (13) and (14). It is seen that in complete accord with theoretical predictions,[17] both entries for the α_2^F are identical but the α_2^K and α_2^N computed with (14) converge variationally more rapidly and with greater accuracy than those computed with (11); in general, this latter effect is enhanced with increasing order. For $N = 540$, the quantities computed with (13) and (14) have converged to the exact RS values within a few units in the last digit reported. Table II displays the nonadiabatic α_j^K, α_j^N, and α_j^F through twentieth order, computed with (13) and (14) for $N = 540$, where the variational convergence determined as illustrated in Table I is again judged to be within a few units in the last digit reported. Table II also collects the previously computed[2] twentieth order α_j for comparison with their components; the partial cancellation of the larger shifts in the components in summing to the α_j is manifest [cf. (15)]. It is highly significant that all (nonvanishing) α_j, and, hence, all α_j^K and α_j^F are positive and all α_j^N are negative. On bearing the definitions (10) of the components in mind, one sees that the physical origins of the nonadiabatic polarizabilities for the ground state of H_2^+ are, *in each order,* unambiguously due to a *decrease* in the average kinetic energy of the molecule coupled with an *increase* in the average (negative) displacement of the electron from the geometric center of the nuclei, these positive contributions being largely offset by the *decrease* in the magnitude of the average nuclear potential of the molecule.

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TABLE II. High-order RS nonadiabatic polarizability components α_j^K, α_j^N, and α_j^F (in atomic units) for the ground state of H_2^+ computed[a] via the PV-RR formalism for $N = 540$.[b]

j	α_j^K	α_j^N	α_j^F	α_j[c]
2	17.491068	−23.321424	11.660712	5.830356
4	15.35165×10^{3}	-21.93093×10^{3}	8.77237×10^{3}	2.19309×10^{3}
6	65.7281×10^{6}	-95.6045×10^{6}	35.8517×10^{6}	5.9753×10^{6}
8	67.550×10^{10}	-99.073×10^{10}	36.027×10^{10}	4.503×10^{10}
10	127.91×10^{14}	-188.50×10^{14}	67.32×10^{14}	6.73×10^{14}
12	38.78×10^{19}	-57.33×10^{19}	20.23×10^{19}	1.69×10^{19}
14	172.3×10^{23}	-255.2×10^{23}	89.3×10^{23}	6.4×10^{23}
16	105.3×10^{28}	-156.2×10^{28}	54.3×10^{28}	3.4×10^{28}
18	84.4×10^{33}	-125.4×10^{33}	43.4×10^{33}	2.4×10^{33}
20	85.4×10^{38}	-127.0×10^{38}	43.8×10^{38}	2.2×10^{38}

[a] Computed with Eqs. (13) and (14).

[b] Field-free expectation values from zero-order virial theorem: $\langle \hat{T} \rangle_0 = 0.597139057$ a.u.; $\langle \hat{V}_0 \rangle_0 = -1.194278114$ a.u.

[c] The total nonadiabatic polarizabilities from Ref. 2; the components are related to the α_j via Eq. (9).

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[3] J. N. Silverman and D. M. Bishop, Chem. Phys. Lett. **130**, 132 (1986).

[4] J. N. Silverman, J. Phys. A **16**, 3417 (1983).

[5] Although the highly accurate non-Born-Oppenheimer calculations of Ref. 2 take nuclear motion into account directly and not as a second step, they are in a certain sense artificial. In correspondence with one of us (D.M.B.), Professor Saul Epstein has pointed out that the Hamiltonian used in Ref. 2 (and here) is not the actual Stark Hamiltonian appropriate to a molecule in a uniform (*laboratory-fixed*) external field, i.e., the perturbing term was taken to be of the form $F\mathbf{r}\cdot\mathbf{R}/|\mathbf{R}|$ rather than $\mathbf{r}\cdot\mathbf{F}$. Nevertheless, these LOPT non-Born-Oppenheimer results do provide the most precise reference point currently available for other model calculations of a related nature (e.g., calculations of α_{zz} in the Born-Oppenheimer approximation) and, for brevity, we refer to them throughout as *nonadiabatic.*

[6] For a recent survey of previous fourth-order nonadiabatic and vibrationally corrected adiabatic results for H_2^+, see D. M. Bishop, J. Pipin, and J. N. Silverman, Mol. Phys. (to be published).

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[13] For a discussion of this issue, see Refs. 2, 3, and 9.

[14] A. D. Buckingham, Adv. Chem. Phys. **12**, 107 (1967). The α_j^s of Eq. (8) are related to the conventional low-order polarizabilities as follows: $\alpha_1^s = \mu_z^{0,s}$, $\alpha_2^s = \alpha_{zz}^s$, $\alpha_3^s = \beta_{zzz}^s$, and $\alpha_4^s = \gamma_{zzzz}^s$.

[15] Application of the Fock scaling procedure [V. Fock, Z Phys. **63**, 855 (1930)] to the exact nonadiabatic expectation value of $\hat{H}$ for an arbitrary diatomic molecule (or atom) yields the nonadiabatic virial theorem, $2\langle\hat{T}\rangle_j^s + \langle\hat{V}_0\rangle_j^s - \langle\hat{H}_1\rangle_{j-1}^s = 0$, which is equivalent to (12); here, of course, the nonadiabatic operators $\hat{T}$, $\hat{V}_0$, and $\hat{H}_1$ must be appropriately defined for the system in hand. Note that (12) and (14) are also applicable to polyatomic molecules if, for example, the electric field is taken parallel to an n-fold axis of rotation.

[16] J. N. Silverman, Int. J. Quantum Chem. **25**, 915 (1984); in the present application, the variable of differentiation is F_z.

[17] The Hellmann-Feynman and virial theorems play fundamentally different roles within the PV-RR formalism. As shown in Refs. 4 and 16, the Hellmann-Feynman theorem, e.g., (13), is precisely satisfied in each order for all states of the exact RS solutions *and* of *arbitrary PV-RR solutions, regardless of the variational* quality of the latter; thus, (11) and (13) will yield the same result for a given $\alpha_j^{F,s}$ and value of N, although, of course, the variational accuracy of this result will improve as N increases. On the other hand, the virial theorem, e.g., (12) and (14), although satisfied in each order for all states of the exact RS solutions, is only satisfied through that order of a given state for which the PV-RR perturbed eigenvector has become quite exact; this is a consequence of the fact that the present PV-RR formalism, Ref. 4, does not employ an overall adjustable scaling parameter. It follows, in general, from their different order dependency that (11) and (14) will, respectively, yield different results for a given j for both $\alpha_j^{K,s}$ and $\alpha_j^{N,s}$ as functions of N, where for a given value of N, the variational accuracy of (14) is superior.

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