

Twentieth-Order Perturbation Study of the Nonadiabatic Electric Polarizabilities for H_2^+ via the Perturbational-Variational Rayleigh-Ritz Formalism

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Large-order perturbation theory has been applied, for the first time, to the Stark effect for H_2^+ , yielding the Rayleigh-Schrödinger ground-state eigenvalue (polarizability) series through twentieth order; previous expansions were limited to fourth order. The calculations were performed nonadiabatically (i.e., without invoking the Born-Oppenheimer approximation) by means of the perturbational-variational Rayleigh-Ritz formalism. The leading terms of the Rayleigh-Schrödinger polarizability series so obtained provide the most accurate values thus far determined for α_{zz} and γ_{zzz} .

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Significant progress has been made during the last few years in the study of hydrogenic ions in external fields via the application of large-order perturbation theory¹ (LOPT); exact or highly accurate solutions of this simpler problem are a prerequisite to a satisfactory treatment of more complex systems. In this context, high-order Stark-effect Rayleigh-Schrödinger (RS) perturbation series have now been obtained²⁻⁶ for the hydrogenic ions; these series are strongly divergent but asymptotic (e.g., see Ref. 1) and, indeed, summable by a variety of techniques.^{1,5,7-9} Such high-order RS eigenvalue series are of considerable theoretical interest *per se* because of the Bender-Wu¹⁰-type asymptotic formulas which can be deduced^{1,3,5,8,11} for the large-order coefficients; further, the series themselves often offer the most convenient practical method of computing physically relevant results^{2,6} because they explicitly contain the field strength as a parameter.

In the present work, we initiate the next logical step in these developments by applying LOPT, for the first time, to the Stark effect for the hydrogen molecular ion, H_2^+ , obtaining the RS eigenvalue (polarizability) series for the ground state through twentieth order; previous calculations¹² have been limited to fourth-order expansions. To obtain results of high accuracy directly, without the necessity of making vibrational corrections, we do *not* invoke the customary Born-Oppenheimer (adiabatic) approximation, but, rather, treat the problem nonadiabatically, viewing H_2^+ as a three-particle system with all particles on an equal footing. Our calculations are made within the framework of the perturbational-variational Rayleigh-Ritz (PV-RR) matrix formalism.¹³⁻¹⁵ Unlike other LOPT methods,¹⁻⁵ which are restricted to hydrogenic systems, the PV-RR formalism can be extended to more complex problems, as in the present case, because it is

based upon the variational principle as well as upon perturbation theory. Although originally developed¹⁵ for the LOPT study of discrete stationary states,^{16,17} it has been shown in a recent study⁶ of the hydrogenic Stark effect that the PV-RR formalism requires no modification when applied to metastable states.¹⁸ Our present results were obtained with a flexible computer program for implementing the PV-RR formalism, which fully exploits the extension to large order via the generalized PV-RR remainder theorem¹⁵; all calculations were performed in ordinary double-precision arithmetic (about sixteen significant digits).

Consider the perturbed nonadiabatic Hamiltonian operator \mathcal{H} for H_2^+ in a uniform electric field F_z parallel to the nuclear (z) axis. In the center-of-mass system, \mathcal{H} can be written as

$$\mathcal{H} = \mathcal{H}(F_z) = \mathcal{H}_0 + \mathcal{H}_1 F_z, \quad (1)$$

where the unperturbed (field free) \mathcal{H}_0 has been fully described in previous nonadiabatic variational calculations.^{19,20} The perturbing (field induced) \mathcal{H}_1 has the form

$$\mathcal{H}_1 = zf, \quad (2a)$$

$$f = 1 + m_e/M \approx 1.000\,272\,234, \quad (2b)$$

where 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 factor²¹ f , of the order of unity, arises from the nonadiabatic treatment of the perturbation. Our goal is to determine the RS series for the perturbed eigenfunctions $|\psi^s(F_z)\rangle$ and eigenvalues $E^s(F_z)$, where the superscript s labels the state. To this end, we introduce a Rayleigh-Ritz *Ansatz* for the $|\psi^s\rangle$ where the basis functions are selected^{12,19,20,22} as

$$|\phi^{uvw}(\xi, \eta, R)\rangle = \exp(-\alpha\xi) \cosh(\beta\eta) \xi^u \eta^v R^{-3/2} \exp(-x^2/2) H_w(x); \quad (3)$$

here, ξ and η are the usual elliptical coordinates of the electron, R is the internuclear distance, $x = \gamma(R - \delta)$, H_w are the Hermite polynomials, α , β , γ , and δ are adjustable state-dependent nonlinear parameters, and u , v , and w

are integers. The *Ansatz* then has the form

$$|\psi^s\rangle = \sum_{u=0}^U \sum_{v=0}^V \sum_{w=0}^W |\phi^{uvw}\rangle C^{s,uvw}, \quad (4)$$

where the linear variational coefficients $C^{s,uvw}$ form a column vector C^s . In the conventional Rayleigh-Ritz approach, one obtains as usual from (4) the matrix eigenvalue equation

$$HC^s = E^s SC^s, \quad (5)$$

where H and S are respectively the total perturbed Hamiltonian and overlap matrices, and E^s and C^s are obtained by numerical diagonalization of (5) for various fixed values of F_z . In the PV-RR procedure, however, H is partitioned according to (1) as

$$H = H(F_z) = H_0 + H_1 F_z, \quad (6)$$

where F_z is treated as a variable perturbing parameter. The application of the PV-RR formalism to (5) and (6) then yields the series

$$C^s = C^s(F_z) = \sum_{j=0}^{\infty} C_j^s F_z^j, \quad (7a)$$

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

to high order for the states of interest in a single computer run. The extent to which the series (7) agree with the corresponding exact RS series depends upon the effective choice⁶ of the basis set, and can be determined, as we shall shortly demonstrate, by an examination of the variational convergence of the individual E_j^s 's. In what follows, we consider only the ground state and suppress the state superscript. Further, to make closer connection to the widely used notation of Buckingham²³ for the lower-order RS static electric polarizabilities, we write the E_j as

$$E_j = -\alpha_j/j!, \quad j = 1, 2, \dots, \quad (8)$$

TABLE I. Variational convergence of PV-RR nonadiabatic α_2 , α_4 , and α_6 (in atomic units) as functions of N .

N	α_2	α_4	$10^{-6}\alpha_6$
26	5.96	1750	1.6
44	5.854	2081	5.1
68	5.837	2149	5.57
100	5.8329	2184	5.86
140	5.8311	2189.7	5.936
190	5.83057	2191.8	5.960
250	5.83043	2192.84	5.9712
320	5.83038	2192.99	5.9738
400	5.83036	2193.05	5.9747
490	5.830357	2193.09	5.9752
540	5.830356	2193.09	5.9753

and refer to the α_j collectively as polarizabilities. For the ground state of a homonuclear diatomic molecule with the electric field parallel to the nuclear axis, the odd-order α_j vanish identically; as a test of our formalism, however, we do not impose this constraint explicitly but numerically compute *all* α_j .

The nonlinear parameters in (3) are fixed at their optimum field-free values²⁰ of $\alpha = 1.6$, $\beta = 0.75$, $\gamma = 3.0$, and $\delta = 2.1$. For various choices of the upper limits U, V, W and suitable constraints on the sum of the indices $u + v + w$, one can systematically construct a sequence of variational eigenfunctions (4) with an increasing number N of basis functions; this is essential in order to test for variational convergence of the α_j (or E_j). Thus, our PV-RR calculations were performed over a wide range of N values, $N = 2, 6, 14, \dots, 400, 490, 540$, where in each case but the last the *Ansatz* contained an equal number²⁴ of even (v restricted to even values) and odd basis functions (v restricted to odd values); for $N = 540$, the constraints are $U = 9$, $V = 13$, $W = 13$, and $u + v + w \leq 13$, which leads to 295 even and 245 odd basis functions. In all calculations, the odd-order α_j were found to vanish identically as required. In Table I are displayed our computed values for α_2 , α_4 , and α_6 as functions of N ; it is seen that for $N = 540$, these quantities have converged to what appear to be the exact RS values within one unit in the last digit reported. Table II collects the α_j through twentieth order obtained for $N = 540$, where the variational convergence, determined as illustrated in Table I, is again judged to be within one unit in the last digit. Although their accuracy does not warrant inclusion in Table II, order-of-magnitude estimates obtained in this manner for α_{22} and α_{24} are respectively 0.2×10^{44} and 0.3×10^{49} . Finally, in Table III, our PV-RR nonadiabatic α_2 and α_4 are compared²³ with polarizabilities (α_{zz}) and hyperpolarizabilities (γ_{zzzz}) computed with more conventional adiabatic (vibrationally corrected) and nonadiabatic methods¹²; these previous results can be further subdivided into variational finite-field^{12,22} (VFF), variational-perturbational²⁵ (VP), and numerical Hartree-Fock²⁶ (NHF) calculations. In all cases, these

TABLE II. High-order RS nonadiabatic polarizabilities α_j (in atomic units) for the ground state of H_2^+ computed via the PV-RR formalism with $N = 540$.^a

j	α_j	j	α_j
2	$0.583\,0356 \times 10$	12	0.169×10^{20}
4	$0.219\,309 \times 10^4$	14	0.64×10^{24}
6	$0.597\,53 \times 10^7$	16	0.34×10^{29}
8	0.4503×10^{11}	18	0.24×10^{34}
10	0.673×10^{15}	20	0.22×10^{39}

^aField-free energy $E_0 = -0.597\,139\,057$ a.u.

TABLE III. Comparison of nonadiabatic α_{zz} and γ_{zzzz} (in atomic units) for H_2^+ computed by different methods.

Method ^a	Type	α_{zz}	$10^{-3}\gamma_{zzzz}$
A	VFF ^b	5.8386	1.502
	VP ^c	5.8386	1.502
B	VFF ^b	5.8386	2.205
	NHF ^d	5.84	2.3
C	VFF ^e	5.8306 ^f	2.27
	VFF ^{b,g}	5.8304 ^f	2.19
	PV-RR ^h	5.830356	2.19309

^aSee Ref. 12: Methods A and B are within the Born-Oppenheimer (adiabatic) approximation with corrections for molecular vibration; method C is non-Born-Oppenheimer (nonadiabatic).

^bReference 12.

^cReferences 12 and 25.

^dReference 26.

^eReference 22; variational $E(F_2)$ fitted with fourth-degree polynomial.

^fCorrected with nonadiabatic f , Eqs. (2).

^gReference 22; variational $E(F_2)$ fitted with even powers of sixth-degree polynomial.

^hThis work.

α_{zz} are in good to excellent agreement with our highly accurate value, the best previous results being obtained^{12,22} via nonadiabatic VFF calculations. The spread among the computed γ_{zzzz} is considerably greater where, again, the nonadiabatic VFF result (computed with the sixth-degree polynomial) is in close agreement with our more accurate value. In the context of methodology, it should be noted that VFF and PV-RR formalisms require essentially the same input matrices, but the former is necessarily limited to lower-order polarizabilities while the latter, with but modest computational effort, is capable of computing with high accuracy the lower-order terms of interest to the experimentalist, as well as higher-order terms required for series summation and theoretical analysis. Further, the prospects of extending the PV-RR formalism to more complex systems, where larger matrices will be required, are distinctly promising since, in the present case, quite good values for α_2 , α_4 , and α_6 were obtained already for $N = 100$ (cf. Table I).

It is of interest to compare the high-order polarizabilities of H_2^+ with those of hydrogenic ions.^{2,6} As might be anticipated, both sets are qualitatively similar. Thus, the α_j for H_2^+ are also strongly divergent but asymptotic (as we have numerically verified). Further, the nonvanishing α_j of H_2^+ have the same sign (all positive) and are of the same order of magnitude as those of H for $0 < j \leq 16$, although for $j \geq 18$ the former are somewhat less violently divergent. We have also computed high-order RS series of a number of expectation values¹⁵ via the PV-RR formalism, including the kinetic- and potential-energy components of the α_j . These, as well as a detailed account of the present work, will be presented elsewhere.

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¹⁸As a result of the unbounded nature of the perturbing potential, the ordinary bound-state variational principle applies to the Stark effect neither for H nor for H_2^+ (although normal bound-state variational behavior is observed for small enough fields); thus, in both cases, the total perturbed problem does not admit L^2 -integrable solutions. Nevertheless, the hierarchy of coupled differential equations of RS perturbation theory do admit L^2 -integrable solutions, and hence, the PV-RR formalism can be used to determine them. Further, the RS eigenvalue series retain their physical validity since, according to the theory of "spectral concentration," they converge, within the limitations of accuracy imposed by their asymptotic character, to the real part of the perturbed complex poles of the Green's function, thus giving the Stark resonance energies; cf. E. C. Titchmarsh, *Eigenfunction Expansions Associated with Second Order Differential Equations* (Oxford Univ. Press, London, 1958), Chap. 20, Pt. II.

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less accurate nonadiabatic polarizability calculations; the effect on the present calculations of omitting f , however, is perceptible and becomes increasingly severe with increasing order since it enters the j th-order polarizability as f^j .

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$\alpha_4 = \gamma_{zzzz}$.

²⁴It follows from symmetry that the even-order eigenvectors (C_0, C_2, \dots) and the odd-order ones (C_1, C_3, \dots) contain respectively only even- and odd-order basis functions. This distribution is achieved automatically via the PV-RR formalism; cf. Ref. 6.

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