

Calculation of high-order electric polarizabilities via the perturbational-variational Rayleigh-Ritz formalism: Application to the hydrogenic Stark effect

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(Received 27 January 1987; revised manuscript received 14 September 1987)

It is demonstrated that perturbation theory combined with the variational principle in the form of the perturbational-variational Rayleigh-Ritz (PV-RR) matrix formalism is a powerful method for applying large-order perturbation theory (LOPT) to the Stark effect for hydrogenic ions. Unlike other more specialized LOPT methods, which do not invoke the variational principle, application of the PV-RR formalism is not restricted to one-electron systems. A paradigm is derived and implemented which permits the precise construction of a Rayleigh-Ritz variational ansatz from which the real Stark ground-state Rayleigh-Schrödinger perturbation series for the eigenfunction, eigenvalue, and arbitrary expectation values can be generated via the PV-RR procedure to any prespecified order in the most economical way possible. A novel method of analysis, based on a combination of the Stark virial, Hellmann-Feynman, and remainder theorems, is developed for studying the physical origins of high-order atomic and molecular polarizabilities; the procedure is illustrated by application to the hydrogenic Stark effect. It is concluded on the basis of this work and of similar high-order PV-RR polarizability calculations for H_2^+ that the prospects for extending the PV-RR formalism to accurate polarizability studies of more complex systems are promising.

I. INTRODUCTION

The Stark effect for hydrogenic ions was the first polarizability phenomenon to be studied in both the old¹ and new²⁻⁴ quantum theory and, indeed, furnished the first example for the application³ of Rayleigh-Schrödinger (RS) perturbation theory. Thus in 1926, the real Stark-effect RS perturbation series for the eigenvalues of arbitrary hydrogenic states was initially determined through first order,^{2,3} and immediately thereafter, through second order,⁴ by several authors independently and almost simultaneously; the extension of these calculations through third order⁵ was not long in following. With an eye to future developments, one should note that these early second- and third-order calculations did not employ *conventional*³ (i.e., spectral sum-over-states) RS perturbation theory⁶ but, rather, were based on analytical methods for obtaining solutions to the hierarchy of coupled inhomogeneous differential equations which arise in a perturbational approach to the Schrödinger equation. Subsequently, however, a method⁷ closely related to conventional RS theory, as well as another procedure⁸ based on the WKB approximation, were used to treat fourth-order effects for arbitrary states, but the correct results were not derived⁹ until 1974 because of the rapid increase in the complexity of the higher-order terms in these approaches. For the ground state, second-order^{10,11} and moderately higher-

order^{12,13} (through tenth-order^{13(b)}) Stark RS eigenvalue series have been available for some time; here again, these results were obtained unconventionally by solution of the RS coupled inhomogeneous differential equations.

The advent of the new discipline of large-order perturbation theory (LOPT), stimulated by the work of Bender and Wu¹⁴ and of Simon¹⁵ on the anharmonic oscillator in the context of quantum field theory, has led to an enormous growth of interest during the last 15 years in calculating very high-order RS eigenvalue series, in summing these series, and in studying the asymptotic behavior of the large-order coefficients. In particular, attention has been focused on LOPT series for a number of important one-particle systems, e.g., the anharmonic oscillator, the Stark and Zeeman effects for hydrogenic ions, and screened Coulomb potentials. Many of these developments are well documented in several recent reviews¹⁶⁻¹⁸ of various aspects of LOPT and its applications. The principal LOPT procedures may be categorized as being based on the Dalgarno-Lewis-Stewart (DLS) *F*-function technique,^{19,6(a),18} logarithmic perturbation theory^{20,17(c),18} (LPT), the hypervirial perturbation method²¹ (HPM), and/or variants of these. The hallmark of all of these LOPT methods is that they completely dispense with the sum-over-states formulation of conventional RS perturbation theory, and, hence, do not require a knowledge of the entire unperturbed spectrum. For example, both the DLS and LPT formalisms²²

represent a return to the spirit of the earlier unconventional calculations^{4,5,10-13} of the Stark effect in that they provide systematic techniques for the direct order-by-order solution (in the one-dimensional case, by quadrature) of the hierarchy of coupled inhomogeneous equations of RS perturbation theory; alternatively, in many cases the inhomogeneous differential equations can be transformed into difference (indicial) equations which can, in turn, be recursively solved by a purely algebraic process.²³

All of these LOPT methods have now been applied (for DLS, LPT, and HPM calculations, see Refs. 24, 25, and 26, respectively) to the Stark effect for hydrogenic ions, yielding RS eigenvalue series to well-nigh arbitrarily high order for the ground and excited states. In view of this success, one might well wonder as to the need for the application of still another LOPT formalism to the hydrogenic Stark problem (which is the subject matter of this paper). In this context, it is significant to note that with the sole exception of the early second-order calculations of Hassé¹⁰ and of Slater and Kirkwood,¹¹ which were based on the variational-perturbational²⁷ method, all other hydrogenic Stark calculations^{2-5,7-9,12,13,24-26} and, indeed, all related LOPT formalisms^{14,16-22} are purely perturbational in nature as they nowhere invoke the variational principle.²⁸ In order to apply LOPT to larger systems, however, it is mandatory to supplement the perturbational approach with variational considerations. Thus, as they stand, these nonvariational LOPT methods, although elegant and powerful, suffer from the grave disadvantage of being restricted²⁹ to one-electron systems (or sums of one-electron operators).

In a recent short communication,³⁰ we have presented preliminary calculations which demonstrate that LOPT can be simply and efficiently applied to the Stark effect for hydrogenic ions via perturbation theory combined with the variational principle in the form of the perturbational-variational Rayleigh-Ritz (PV-RR) matrix formalism³¹⁻³³. The present paper is devoted to a detailed account of the ideas and methods introduced in Ref. 30, and several new results are added; as in Refs. 24, 25(b), and 26, we limit ourselves throughout to LOPT calculations of the real part of the Stark resonance energies³⁴. It should be noted that unlike the nonvariational LOPT formalisms, the PV-RR formalism can be extended to larger systems. Thus, in addition to the classical calculation of normal modes in oscillating astrophysical systems,^{31,35} the PV-RR approach has been applied to generate high-order atomic $1/Z$ expansions for the helium isoelectronic sequence,³⁶ and high-order RS series of molecular-orbital eigenvalues in topological studies of several organic molecules.³⁷⁻³⁹ Most recently, high-order electric polarizabilities for the hydrogen molecular ion H_2^+ have been determined⁴⁰⁻⁴³ via the PV-RR formalism where both a non-Born-Oppenheimer^{40,42,43} (20th-order) and Born-Oppenheimer⁴¹ (30th-order) polarizability series were computed; previous polarizability expansions for H_2^+ were limited to fourth order.⁴⁴ We regard these calculations for H_2^+ , as well as the present results for the hy-

drogenic Stark effect where a wealth of accurate high-order comparative data is available, as providing a severe proving ground for the applicability of the PV-RR formalism to compute high-order atomic and molecular polarizabilities. In this context, we stress that the PV-RR formalism was originally developed to deal with bound states and convergent RS series, while the Stark effect is characterized by metastable states⁴⁵ and strongly divergent but asymptotic RS series [see, e.g., Ref. 17(a)]; as we shall demonstrate, however, the PV-RR formalism is immediately applicable without any modification to this more demanding situation.

This paper is organized as follows. In Sec. II the theory of the Stark effect for hydrogenic ions is summarized. In addition to the usual RS series of the eigenfunction and eigenvalue, high-order RS series of the kinetic, nuclear-potential, and field-potential energetic components of the eigenvalue are also considered. In particular, it is shown that the RS eigenvalue perturbational corrections in each order result from the delicate partial balancing of larger opposing perturbational corrections in their kinetic, nuclear-potential, and field-potential components, where the relative magnitudes and signs of these component shifts are precisely determined by general *a priori* constraints; this method of analysis, which can be extended to arbitrary atoms and diatomic molecules, gives considerable insight into the physical origins⁴³ of electric polarizabilities. Furthermore, the Bender-Wu-type¹⁴ asymptotic formulas are derived which govern the limiting behavior of the large-order coefficients of the various energetic components of the eigenvalue; these results are of theoretical interest *per se*. In Sec. III the PV-RR formalism and its application to the hydrogenic Stark effect are briefly described; the role of the ordinary variational principle in the Stark PV-RR calculations is discussed. A paradigm is derived, which permits the precise construction of a Rayleigh-Ritz (RR) variational ansatz from which the real Stark RS ground-state eigenfunction and eigenvalue series can be generated via the PV-RR formalism to any prespecified order in the most economical way possible. Two independent PV-RR methods for computing high-order RS series of the kinetic, nuclear-potential, and field-potential energetic components of the eigenvalue are described and compared. In Sec. IV the results of our LOPT Stark PV-RR calculations are reported and discussed. Finally, in Sec. V our conclusions are presented.

II. THE STARK EFFECT FOR HYDROGENIC IONS

Consider the perturbed Schrödinger equation for a hydrogenic ion of nuclear charge Z in a uniform electrostatic field of strength F parallel to the z axis,

$$(\mathcal{H} - \epsilon^s) |\psi^s\rangle = 0, \quad s = 1, 2, \dots \quad (1)$$

where \mathcal{H} is the perturbed Hamiltonian operator, $|\psi^s\rangle$ and ϵ^s are, respectively, the perturbed exact normalized eigenfunction and eigenvalue of the s th state. If spin and relativistic effects are neglected, \mathcal{H} in Z -scaled a.u. (unit of length, Z^{-1} a.u.; unit of energy, Z^2 a.u.; unit of

field strength, Z^3 a.u.) can be written in the linearly perturbed form

$$\mathcal{H} = \mathcal{H}(\lambda) = \mathcal{H}_0 + \mathcal{H}_1 \lambda ; \quad (2)$$

here the unperturbed (field-free) \mathcal{H}_0 , and the kinetic and nuclear-potential operators, \mathcal{T} and \mathcal{V}_0 , respectively, are given by

$$\mathcal{H}_0 = \mathcal{T} + \mathcal{V}_0 , \quad (3)$$

$$\mathcal{T} = -\frac{1}{2} \nabla^2 , \quad (4a)$$

$$\mathcal{V}_0 = -r^{-1} , \quad (4b)$$

and the perturbing (field-induced) \mathcal{H}_1 and the coupling parameter λ by

$$\mathcal{H}_1 = z = r \cos \theta , \quad (4c)$$

$$\lambda = F/Z^3 . \quad (4d)$$

Unlike the great majority of other calculations of the hydrogenic Stark effect, we shall work throughout in spherical coordinates as this permits the direct PV-RR determination of the RS series of the eigenfunction, eigenvalue, and associated expectation values. In the present PV-RR calculations, therefore, we completely dispense with the complications [see, e.g., Ref. 24(a)] entailed in separating (1) in parabolic coordinates and then computing the auxiliary RS series of the separation constants, as is customarily done; moreover, the use of spherical coordinates⁴⁶ will facilitate the extension of our procedure to larger systems which are not separable in parabolic coordinates.

In general, we seek to high order the real RS series

$$|\psi^s\rangle = |\psi^s(\lambda)\rangle = \sum_{j=0}^{\infty} |\psi_j^s\rangle \lambda^j , \quad (5a)$$

$$\varepsilon^s = \varepsilon^s(\lambda) = \sum_{j=0}^{\infty} \varepsilon_j^s \lambda^j ; \quad (5b)$$

in particular, in this exploratory study of the applicability of the PV-RR formalism to LOPT polarizability calculations, we focus our attention on the ground state ($s=1$) for which highly accurate large-order results are available^{24(a),25(b)} for comparison. In LOPT polarizability studies, it is convenient to rewrite (5b) as⁴⁷

$$\varepsilon^s = \varepsilon_0^s - \sum_{j=1}^{\infty} (j!)^{-1} \alpha_j^s \lambda^j , \quad (6a)$$

$$\alpha_j^s = -j! \varepsilon_j^s , \quad j=1,2,\dots , \quad (6b)$$

thereby defining, in this notation, the permanent dipole moment α_1^s , the (customary) polarizability α_2^s , the first and second hyperpolarizabilities, α_3^s and α_4^s , respectively, etc. For the most part, we shall present our results in terms of (5b), although occasionally we shall employ (6) and, for convenience, refer to the α_j^s collectively for all j as polarizabilities.

We also seek to high order the real RS series of the kinetic, nuclear-potential, and field-potential components [$\langle \mathcal{T} \rangle^s(\lambda)$, $\langle \mathcal{V}_0 \rangle^s(\lambda)$, and $\langle \mathcal{H}_1 \rangle^s(\lambda)$, respectively] of the eigenvalue,

$$\langle \mathcal{A} \rangle^s = \langle \mathcal{A} \rangle^s(\lambda) = \sum_{j=0}^{\infty} \langle \mathcal{A} \rangle_j^s \lambda^j , \quad \mathcal{A} = \mathcal{T}, \mathcal{V}_0, \mathcal{H}_1 , \quad (7)$$

where, in general, $\langle \mathcal{A} \rangle^s$ denotes the expectation value for the s th state of an arbitrary operator \mathcal{A} independent of λ ,

$$\langle \mathcal{A} \rangle^s(\lambda) = \langle \psi^s(\lambda) | \mathcal{A} | \psi^s(\lambda) \rangle , \quad (8a)$$

with RS perturbation-series coefficients,

$$\langle \mathcal{A} \rangle_j^s = \sum_{k=0}^j \langle \psi_k^s | \mathcal{A} | \psi_{j-k}^s \rangle , \quad j=0,1,\dots . \quad (8b)$$

From (1)–(3), (5), and (7), we have

$$\varepsilon^s = \langle \mathcal{T} \rangle^s + \langle \mathcal{V}_0 \rangle^s + \langle \mathcal{H}_1 \rangle^s \lambda \quad (9a)$$

and

$$\varepsilon_j^s = \langle \mathcal{T} \rangle_j^s + \langle \mathcal{V}_0 \rangle_j^s + \langle \mathcal{H}_1 \rangle_{j-1}^s , \quad j=0,1,\dots . \quad (9b)$$

In analogy with (6), it is useful to express the α_j^s as the sum of the energetic components by rewriting (9b) in the alternative form,⁴³

$$\alpha_j^s = \alpha_j^{K,s} + \alpha_j^{N,s} + \alpha_j^{F,s} , \quad j=1,2,\dots . \quad (10)$$

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

$$\alpha_j^{K,s} = -j! \langle \mathcal{T} \rangle_j^s , \quad (11a)$$

$$\alpha_j^{N,s} = -j! \langle \mathcal{V}_0 \rangle_j^s , \quad (11b)$$

$$\alpha_j^{F,s} = -j! \langle \mathcal{H}_1 \rangle_{j-1}^s . \quad (11c)$$

Once the RS series of the eigenfunction, Eq. (5a), has been determined, the RS series of an arbitrary expectation value, Eq. (7), can be computed with (8b). In the special case, however, of the components of the α_j^s (or ε_j^s), Eqs. (10) and (11), it is advantageous to derive new relationships between the *individual* components and the total polarizabilities via the Stark-effect virial and Hellmann-Feynman theorems. The Stark virial theorem

$$2 \langle \mathcal{T} \rangle^s + \langle \mathcal{V}_0 \rangle^s - \langle \mathcal{H}_1 \rangle^s \lambda = 0 , \quad (12)$$

readily follows from the Fock⁴⁸ scaling procedure. Further, if one treats λ as the variable of differentiation, the Hellmann-Feynman theorem has the form

$$\partial \varepsilon^s / \partial \lambda = \langle \mathcal{H}_1 \rangle^s . \quad (13)$$

The expansion of (12) and (13) in powers of λ then yields, respectively, for $j=1,2,\dots$,

$$2\alpha_j^{K,s} + \alpha_j^{N,s} - \alpha_j^{F,s} = 0 , \quad (14)$$

and

$$\alpha_j^{F,s} = j \alpha_j^s . \quad (15)$$

On combining (10), (14), and (15), one obtains

$$\alpha_j^{K,s} = (2j-1) \alpha_j^s , \quad (16a)$$

$$\alpha_j^{N,s} = (2-3j) \alpha_j^s . \quad (16b)$$

Thus Eqs. (15) and (16), which also hold (when the operators are properly defined⁴⁹) for the exact RS polarizabilities of all states of all atoms and, in certain cases, for diatomic molecules,⁴³ completely separate the components and permit their indirect theoretical determination via the α_j^s (or ε_j^s); in view of the fundamentally different roles of the Hellmann-Feynman⁵⁰ and virial theorems in the PV-RR formalism (cf. Sec. III D), it is significant to note that (15) depends only upon the former theorem while (16) results from combining both theorems. Equations (15) and (16) display quantitatively the previously mentioned delicate partial balancing of the components which we have established here in an *a priori* manner. These relationships impose severe constraints on the relative magnitudes and signs of the components. In general, for $j \geq 2$, it follows that $|\alpha_j^{N,s}| > |\alpha_j^{K,s}| > |\alpha_j^{F,s}| > |\alpha_j^s|$, 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 opposite sign; thus, we can write

$$|\alpha_j^s| = | |\alpha_j^{K,s} + \alpha_j^{F,s}| - |\alpha_j^{N,s}| |, \quad j = 1, 2, \dots \quad (17)$$

Moreover, from the known⁵¹ asymptotic behavior of the large-order ε_j^s in the hydrogenic Stark effect, we can also read off from (15) and (16) the Bender-Wu-type asymptotic formulas for the individual energetic components. For example, for the ground state, where only the even-order α_{2j}^1 are nonvanishing, one obtains [cf. Ref. 51(c)] in obvious notation,

$$\begin{aligned} \alpha_{2j}^{X,1} &\sim f_X(j) 6\pi^{-1} \left(\frac{2}{3}\right)^{2j} [(2j)!]^2 \\ &\times [1 + (\frac{2}{3})A_{00}(2j)^{-1} + (\frac{2}{3})^2 B_{00}(2j)^{-1}(2j-1)^{-1} \\ &+ O(j^{-3})], \end{aligned} \quad (18a)$$

where

$$f_X(j) = (4j-1), \quad 2(1-3j), \quad 2j \quad \text{for } X = K, N, F, \quad (18b)$$

respectively, and $A_{00} = -8.916$, $B_{00} = 25.57 \dots$

In Sec. I we alluded to the metastable character of the perturbed Stark states; we conclude this section with a brief summary of some of the associated pathological aspects of the Stark effect as opposed to ordinary bound-state behavior.

(1) In principle, as has long been recognized,⁴⁵ it follows from the unbounded nature of the perturbing potential \mathcal{H}_1 that for any real nonzero value of λ (or F), no matter how small its magnitude, the discrete hydrogenic spectrum of \mathcal{H}_0 dissolves into a continuum ranging from $-\infty$ to ∞ ; in practice, however, for small λ , the perturbed Stark states are quasi-stationary (weakly quantized) since it takes a very long time for the initially bound electron to tunnel through the potential barrier to the outer region. In the same context, the ordinary bound-state variational principle does not apply (see, e.g., Refs. 16 and 52) to the Stark effect because continuum states cannot be exactly represented by L^2 -integrable

basis functions, although for small enough field strengths and/or variational matrices, normal bound-state variational behavior is simulated.^{52,53} This latter phenomenon has been made the basis of the so-called "stabilization" method⁵³ for attempting to overcome the failure of the ordinary variational principle; we return to this point in Sec. III B, where the behavior of conventional variational calculations for the Stark effect is compared to that of corresponding PV-RR calculations. Although outside the scope of the present LOPT study, it should be noted that a number of nonperturbative approaches, which are independent of the ordinary variational principle, are also available for Stark calculations; these include the power-series boundary-condition method,⁵⁴ Weyl's m -function technique,⁵⁵ the minimum-variance principle,^{52(a)} and the use of complex coordinates.^{51(c),56}

(2) The Stark perturbation is singular because of the abrupt change in the nature of the eigenvalue spectrum when the field is applied; hence, the RS eigenvalue series (5b) are strongly divergent⁵⁷ [the ε_{2j}^1 diverge factorially as $(2j)!$, cf. Eq. (18a)]. Nevertheless, paradoxically, the real ε_j^s contain all the information^{51,57-61} required to compute the complex Stark eigenvalues (resonances) to high accuracy. In this context, the series (5b) are asymptotic and Borel summable about imaginary fields.⁵⁷ Moreover, the partial sums of (5b) assume physical significance via the concept of "spectral concentration."⁵⁸ Thus one may view the onset of the continuum as corresponding to the movement of the poles of the Green's function off the negative real axis, where they correspond to the unperturbed discrete hydrogenic spectrum, down into the complex plane, where they become Stark resonances.⁵⁷ The real part of the complex poles gives the real part of the Stark resonances to which the real RS eigenvalue series converge within the limitations of accuracy⁶² imposed by their asymptotic character. Because of the simplicity of the procedure, partial conventional summation of (5b) over a range of field strengths offers a convenient method of computing Stark energy shifts induced by smaller fields, and accurate results have been obtained^{24(a)} in this manner. Furthermore, it has been shown^{57,59,60} that the widths (ionization rates) of the Stark resonances, which are given by the imaginary parts of the complex poles, can be precisely extracted from the ε_j^s by analytic continuation combined with various summation techniques;⁶¹ simultaneously, these summation-continuation procedures also yield^{59,60} accurate values of the real part of the resonances for larger values of the field strength. These results demonstrate the central role of the real RS eigenvalue series (5b).

(3) It is evident from Eqs. (15) and (16) that the RS series of the energetic components of the Stark eigenvalues are also strongly divergent (indeed, more so than the eigenvalue series); we have, however, verified numerically for the ground state that they converge asymptotically (as anticipated) to the real part of the corresponding expectation values. Thus, for small fields, these RS eigenvalue-component series have the same practical computational value as the eigenvalue series.

III. APPLICATION OF THE PV-RR FORMALISM TO THE STARK EFFECT

A. Preliminaries

The generalized PV-RR procedure³³ strengthens and extends to large order earlier quantum-mechanical matrix formulations⁶³ of RS perturbation theory. Although the basic idea is not new, many of the details of the PV-RR formalism and of its implementation are. In general, the PV-RR formalism cleanly extracts to high order the "perturbational content" of a given perturbed variational matrix eigenvalue equation for either classical or quantum-mechanical systems. The specific nature of this perturbational content depends, of course, upon the choice of the unperturbed matrix eigenvalue equation taken as a zeroth-order reference system, where in the PV-RR formalism, unlike conventional RS perturbation theory, this choice is almost completely at our disposal, e.g., Refs. 36–39.

For an arbitrary M -electron system, one prepares the way⁶⁴ for PV-RR calculations by introducing a Rayleigh-Ritz (RR) or configuration-interaction ansatz for the eigenfunction $|\psi^s\rangle$,

$$|\psi^s\rangle = \sum_{t=1}^N |\phi^t\rangle C^{ts}, \quad (19)$$

where the summation is over, say, N M -electron antisymmetric functions $|\phi^t\rangle$ of appropriate symmetry, and the C^{ts} are linear variational coefficients which form a column eigenvector \mathbf{C}^s ; the $|\phi^t\rangle$ are constructed in the usual manner from an arbitrary complete discrete basis of λ -independent, L^2 -integrable one-electron functions (spin orbitals) which may, but need not, be orthonormal. For a one-electron system, the $|\phi^t\rangle$ are themselves the basis functions, which in the present case of the ground state ($m=0$) of the hydrogenic Stark effect we take to be the discrete orthonormal basis,

$$|\phi^t\rangle = |n\ell 0\rangle = R_{n\ell}(r) Y_{\ell 0}(\theta, \phi), \quad (20)$$

where the normalized radial functions $R_{n\ell}(r)$ are the associated Laguerre functions of order $2\ell+2$,

$$R_{n\ell}(r) = [2/(n+\ell+1)!]^{3/2} [(n-\ell-1)!]^{1/2} \times (2r)^\ell L_{n+\ell+1}^{2\ell+2}(2r) e^{-r} \quad (21)$$

(the overall scaling parameter is fixed at unity), the $L_{n+\ell+1}^{2\ell+2}(2r)$ are the associated Laguerre polynomials of order $2\ell+2$ and degree $n-\ell-1$, and the $Y_{\ell 0}(\theta, \phi)$ are the usual normalized spherical harmonics. The use of (21) has long been advocated⁶⁵ in atomic RR calculations because, unlike the hydrogenic radial eigenfunctions which they closely resemble (the $|1s\rangle$ function is identical in both sets), the former constitute a complete discrete basis without continuum contributions; furthermore, the evaluation of all integrals in this basis by generating-function techniques⁶⁶ is straightforward. The proper selection of the n, ℓ distribution of the orbitals [Eq. (20)] in constructing (19) is essential in obtaining accurate perturbational results, and in Sec. III C we derive a prescription for this via the PV-RR formalism which

enables the calculation of the exact RS $|\psi_j^1\rangle$ and ϵ_j^1 through arbitrarily high order. If one were to pursue the customary RR approach, one would assign a numerical value to λ in (2) in order to obtain the matrix eigenvalue equation

$$\mathbf{H}\mathbf{C}_{\text{RR}}^s = \epsilon_{\text{RR}}^s \mathbf{C}_{\text{RR}}^s, \quad (22)$$

where \mathbf{H} is the total perturbed Hamiltonian matrix, and \mathbf{C}_{RR}^s and ϵ_{RR}^s denote the RR approximations to the exact eigenvectors \mathbf{C}^s and eigenvalues ϵ^s , respectively, which would be obtained by standard numerical diagonalization of \mathbf{H} for various fixed values of λ . In the PV-RR approach, however, in marked contrast to the RR procedure, \mathbf{H} is partitioned according to (2) as

$$\mathbf{H} = \mathbf{H}(\lambda) = \mathbf{H}_0 + \mathbf{H}_1 \lambda, \quad (23)$$

$$\mathbf{H}_0 = [H_0^{ts}], \quad (24a)$$

$$H_0^{ts} = \langle \phi^t | \mathcal{H}_0 | \phi^s \rangle, \quad (24b)$$

$$\mathbf{H}_1 = [H_1^{ts}], \quad (24c)$$

$$H_1^{ts} = \langle \phi^t | \mathcal{H}_1 | \phi^s \rangle, \quad (24d)$$

where λ is not assigned fixed numerical values, but, rather, treated as a variable perturbing parameter. Application of the PV-RR procedure to (22) and (23), constructed with the proper choice of orbitals, then yields the exact real RS eigenvector, eigenfunction, and eigenvalue series,

$$\mathbf{C}^1 = \mathbf{C}^1(\lambda) = \sum_{j=0}^{\infty} \mathbf{C}_j^1 \lambda^j, \quad (25a)$$

$$|\psi^1\rangle = |\psi^1(\lambda)\rangle = \sum_{j=0}^{\infty} |\psi_j^1\rangle \lambda^j, \quad (25b)$$

$$|\psi_j^1\rangle = \sum_{t=1}^N |\phi^t\rangle C_j^{t1}, \quad (25c)$$

$$\epsilon^1 = \epsilon^1(\lambda) = \sum_{j=0}^{\infty} \epsilon_j^1 \lambda^j, \quad (25d)$$

as well as the associated real RS expectation-value series,

$$\langle \mathcal{A} \rangle^1 = \langle \mathcal{A} \rangle^1(\lambda) = \sum_{j=0}^{\infty} \langle \mathcal{A} \rangle_j^1 \lambda^j, \quad \mathcal{A} = \mathcal{T}_1, \mathcal{V}_0, \mathcal{H}_1, \quad (25e)$$

to high order for the ground state in a single computer run. These calculations are feasible because the large-order cyclic PV-RR formalism, which embodies a number of algorithms incorporating the basic procedure augmented by the generalized PV-RR remainder,³³ Hellmann-Feynman,⁵⁰ and Stark virial³⁰ theorems, is extremely compact and completely avoids the explicit cumbersome formulations of conventional RS perturbation theory.

B. Validity of the ordinary variational principle

It is appropriate to compare and contrast the role of the variational principle in the conventional RR procedure and in the present PV-RR calculations. It has al-

ready been noted in Sec. II that the ordinary variational principle does not apply to the metastable states encountered in the Stark effect: Hence, unlike bound-state calculations, the ϵ_{RR}^s obtained via numerical diagonalization of (22) for fixed values of λ do not satisfy the Hylleraas-Undheim-MacDonald theorem⁶⁷ in the sense that one cannot be assured that for all N and λ , $\epsilon_{RR}^s \geq \epsilon^s$, $s = 1, 2, \dots, N$, or that the ϵ_{RR}^s for fixed λ monotonically approach the exact resonance energies ϵ^s from above as $N \rightarrow \infty$. For very small λ (this permissible range of λ is basis, N , and state dependent), normal bound-state variational behavior is observed, but for fixed N and increasing λ , or vice versa, a series of avoided crossings invariably take place,^{52(b),52(c)} where, for example, if we consider the ground state, ϵ_{RR}^1 ceases to be an upper bound to ϵ^1 but diverges abruptly below it to large negative values, being replaced by ϵ_{RR}^2 as an upper bound to ϵ^1 , after which ϵ_{RR}^2 also diverges in turn, etc. Although, as previously mentioned, this stabilization phenomenon of successive, temporarily stable approximations can be exploited⁵³ to give good to fair estimates of the lowest real Stark eigenvalues for small λ , the procedure becomes increasingly inaccurate and difficult to implement^{52(b)} for larger λ .

The variational collapse of RR calculations for the Stark effect is, however, completely obviated by the PV-RR procedure: Although (1) does not admit exact or approximate L^2 -integrable solutions, it has been found^{30,40-43} that Stark PV-RR series can be computed from (22) and (23) constructed with an L^2 -integrable basis, in precisely the same manner as if one were dealing with a bound state. Thus the PV-RR series coefficients converge variationally with increasing N in a stable manner to the corresponding exact RS coefficients. It should be noted, however, that, in general, individual coefficients of the PV-RR eigenvalue series are *not* upper bounds⁶⁸ to the equivalent terms of the RS series; this applies to both bound states and metastable states. Despite the absence of a minimal principle in each order, the extent to which the PV-RR eigenvalue, eigenfunction, and expectation-value series agree with the corresponding exact RS series depends upon the effective choice and degree of saturation of the basis set, and can be readily monitored as a function of increasing N by examining^{30,40-43} the (possibly nonmonotonic) variational convergence of the individual PV-RR series coefficients; this is the basis of the procedure used in Sec. III C to derive a paradigm for constructing the exact RS $|\psi_j^1\rangle$ via the PV-RR procedure.

Qualitatively, the above behavior finds explanation in the theory of spectral concentration.⁵⁸ The fact that the Stark perturbation series retain their physical significance implies that the exact $|\psi_k^s\rangle$, $k = 1, 2, \dots$, solutions of the hierarchy of RS coupled inhomogeneous equations, are L^2 integrable in the sense that the RS integrals over the $|\psi_k^s\rangle$, which define the ϵ_j^s are convergent; this is in harmony, for example, with the observation^{12,13(b)} that the $|\psi_k^1\rangle$ for the hydrogenic Stark effect consist of a finite linear combination (FLC) of the product of truncated polynomials of r and various Legendre polynomials with an overall factor of a hydro-

genic $|1s\rangle$ eigenfunction. We conclude that although a global variational principle does not apply to (1) in the form of (22) with fixed λ , the order-by-order calculation of variational approximations to the $|\psi_k^s\rangle$ and ϵ_j^s via the solution of the corresponding PV-RR coupled inhomogeneous matrix equations, obtained³³ by series expansion of (22), is valid. Furthermore, the partial sums of the RS eigenvalue and eigenvector series, or equivalently, of their accurate variational approximations obtained via the PV-RR method, do not display the anomalous behavior of switching states (avoided crossings) associated with the corresponding RR calculations, but, instead, converge asymptotically to the proper state limits; this contrasting behavior of Stark PV-RR and RR calculations is demonstrated in Sec. IV.

C. Construction of the exact RS $|\psi_j^1\rangle$

It is essential in the PV-RR procedure to construct a systematic sequence of RR trial eigenfunctions with increasing N in order to test for variational convergence of the individual ϵ_j^s , Eq. (5b), and $\langle \mathcal{A} \rangle_j^s$, Eq. (7). Normally, it would be entirely adequate to proceed in analogy with previous PV-RR calculations⁴⁰⁻⁴³ by including in (19) gradually increasing numbers of the different n, ℓ types of orbitals [Eq. (20)]. In the present case, however, we can find via the PV-RR formalism a prescription for the construction of the *optimum* ansatz [Eq. (19)] which enables one to generate the exact RS $|\psi_j^1\rangle$ and ϵ_{2j}^1 to any prespecified order in the most economical way possible. We start by noting that the matrix elements (24) are subject to severe selection rules due to symmetry. Thus \mathbf{H}_0 is block diagonal in ℓ , which greatly reduces the computational labor of the PV-RR zeroth-order calculations.³³ Furthermore, H_{ts}^1 vanishes unless $t = n, \ell, 0$ and $s = n, \ell \pm 1, 0$ or $s = n \pm 1, \ell \pm 1, 0$; these selection rules for \mathbf{H}_1 furnish the necessary clue for deriving the prescription. From these rules and the RS (and PV-RR) equations defining the ϵ_j^1 , we infer that given $|\psi_0^1\rangle = |1s\rangle$ (which follows from our choice of orbitals), $|\psi_1^1\rangle$ must be a FLC of $\ell = 1$ orbitals, $|\psi_2^1\rangle$ a FLC of $\ell = 0, 2$ orbitals, \dots , $|\psi_{2k}^1\rangle$ a FLC of $0, 2, 4, \dots, 2k$, and $|\psi_{2k+1}^1\rangle$ a FLC of $\ell = 1, 3, 5, \dots, 2k + 1$, where $k = 0, 1, \dots$; evidently, for arbitrary $|\psi_j^1\rangle$, we have $\ell_{\max} = j$, where ℓ_{\max} is the maximum value of ℓ which occurs. The specific n, ℓ distribution of the orbitals cannot be obtained in a completely *a priori* manner since it is basis independent. To make further progress, we use the PV-RR formalism as a sensitive analytical tool. Thus, in an order-by-order manner, we systematically *oversaturate* the ansatz and inspect the elements of the perturbed eigenvectors C_j^{t1} , $t = 1, 2, \dots, N$, rejecting those orbitals for which the corresponding eigenvector elements either vanish identically or are vanishingly small; this is feasible because the PV-RR procedure automatically samples the contribution in each order of each of the N orbitals. Simultaneously, one examines the ϵ_{2j}^1 (which are obtained from the C_i^1 , $i = 0, 1, \dots, j$, via the generalized PV-RR remainder theorem³³) for variational saturation. In this manner, the following paradigm was derived by induction: For

$k=0, 1, \dots$, the orbitals [Eq. (20)] required to construct the RS $|\psi_{2k}^1\rangle$ exactly are

$$N_\ell(2k) = 4k + 1 - \ell, \quad \ell = 0, 2, \dots, 2k, \quad (26a)$$

and to construct the RS $|\psi_{2k+1}^1\rangle$,

$$N_\ell(2k+1) = 4k + 3 - \ell, \quad \ell = 1, 3, \dots, 2k+1. \quad (26b)$$

Here, N_ℓ denotes the number of orbitals with the subindexed common value of ℓ with values of n varying over the range $n = \ell + 1, \ell + 2, \dots, \ell + N_\ell$. The optimum total number of orbitals N , distributed in accordance with (26) and required to compute the RS series (25) correctly through $|\psi_{2k}^1\rangle$ and ε_{4k+1}^1 , are then

$$\begin{aligned} N(2k, 4k+1) &= \sum_{q=0}^k N_{2q}(2k) + \sum_{q=0}^{k-1} N_{2q+1}(2k+1) \\ &= 6k^2 + 3k + 1, \end{aligned} \quad (27a)$$

and through $|\psi_{2k+1}^1\rangle$ and ε_{4k+3}^1 ,

$$\begin{aligned} N(2k+1, 4k+3) &= \sum_{q=0}^k [N_{2q}(2k) + N_{2q+1}(2k+1)] \\ &= 6k^2 + 9k + 3. \end{aligned} \quad (27b)$$

Thus each optimum $N(j, 2j+1)$ defined by (26) and (27) has associated with it an n, ℓ distribution which is used to construct the corresponding RR ansatz [Eq. (19)], e.g., for $N(2k+1, 4k+3)$, this distribution is given by $N_0(2k), N_1(2k+1), N_2(2k), \dots, N_{2k+1}(2k+1)$; note that (26) also gives the dimensions of the largest ℓ block in \mathbf{H}_0 for a given choice of N , namely, $N_0(2k) = 4k + 1$ for $N(2k, 4k+1)$ and $N_1(2k+1) = 4k + 2$ for $N(2k+1, 4k+3)$.

D. The energetic components of the α_j^s

As described in Sec. II, our method of analysis of the physical origins of the high-order α_j^s is based upon the resolution of the polarizabilities into their energetic components [cf. Eq. (10)]. Two independent methods of computing the latter via the PV-RR formalism are available: (1) From the basic PV-RR formalism,³³ as with the expectation value of any λ -independent operator, we have the purely numerical procedure,

$$\langle \mathcal{A} \rangle_j^s = \sum_{k=0}^j \mathbf{C}_k^{s\dagger} \mathbf{A} \mathbf{C}_{j-k}^s, \quad \mathbf{A} = \mathbf{T}, \mathbf{V}_0, \mathbf{H}_1, \quad (28)$$

the matrix equivalent of (8b), which together with (11), yields the components directly; here \mathbf{A} is the matrix representation of \mathcal{A} in the chosen basis (20). (2) Alternatively, we also have the Hellmann-Feynman and Stark virial theorems at our disposal, where the former leads to (15), and both theorems combined lead to (16); these *a priori* relationships completely separate the $\alpha_j^{K,s}$, $\alpha_j^{N,s}$, and $\alpha_j^{F,s}$, and permit them to be expressed individually as simple order-dependent multiples of the α_j^s .

Note that if (28) is used, a knowledge of the RS eigen-

vector series (25a) through $(2n+1)$ th order is required to compute the RS component series (25e) through like order; with (15) and (16), however, the component series can be determined through $(2n+1)$ th order, with but negligible computational effort, from the n th-order eigenvector series since the latter yields the eigenvalue series (25d) through $(2n+1)$ th order via the PV-RR remainder theorem.³³ In the present case, where the exact RS α_j^1 (or ε_j^1) can be determined to arbitrarily high order via the paradigm of (26) and (27), the use of (15) and (16), rather than (28), is to be preferred because of the *a priori* theoretical insight so obtained plus the considerable reduction in computational labor.

Nevertheless, it is of some theoretical and practical interest to analyze in greater detail the distinction between the results computed with the two methods. The Hellmann-Feynman theorem is precisely satisfied^{33,50} in each order of all states of the exact RS solutions and of arbitrary PV-RR solutions, regardless of the variational quality of the latter; hence, (28) and (15) are constrained to yield identical PV-RR results for a given $\alpha_j^{F,s}$ and value of N , and no conclusions can be drawn from this equality concerning the exactness of the corresponding j th-order PV-RR eigenvector series. In contrast, the virial theorem, although satisfied in each order for all states of the exact RS solutions, is only satisfied in the PV-RR formalism through that order of a given state for which the PV-RR eigenvector series has become *quite exact* with increasing N ; this is a consequence of the fact that the present PV-RR formalism does not employ an overall scaling parameter to force satisfaction of the virial theorem in each order. In general, it follows that for smaller N , the virial theorem will not be satisfied in higher order so that (28) and (16), due to their different order dependency on the eigenvector series, will yield different PV-RR results for a given (larger) j and value of N for both $\alpha_j^{K,s}$ and $\alpha_j^{N,s}$, where the variational accuracy of (16) will be somewhat greater; as N increases, the $\alpha_j^{K,s}$ and $\alpha_j^{N,s}$ computed with (16) will converge more rapidly to their respective exact RS limits than the corresponding values computed with (28); when the latter have converged, the virial theorem will be satisfied with good accuracy through j th order. In this context, (28) furnishes a useful supplementary criterion for the variational accuracy of the PV-RR eigenvector series, as well as a general check on the consistency of the PV-RR calculations; such an application is illustrated in Sec. IV.

IV. RESULTS AND DISCUSSION

In the present work we have extended our preliminary PV-RR study³⁰ of the ground state of the hydrogenic Stark effect to the wide range of optimum N values from $N=3(1,2)$ to $N=459(17,35)$. The calculations were performed in ordinary double-precision arithmetic (about 16 significant digits) with a flexible computer program for implementing the PV-RR formalism, which incorporates all PV-RR algorithms and theorems; a key feature is the extension to large order via the generalized PV-RR remainder theorem.³³ In all computations, the odd-order ε_j^1 were found to vanish identically as re-

quired,⁴⁷ although, as a test of our formalism, this constraint was not explicitly imposed.

In the first phase of our study, we have subjected the paradigm of (26) and (27) to exhaustive tests. In general, all of our results are in complete harmony with the paradigm. Typical calculations of this type are collected in Table I, which exhibits the variational convergence to the exact RS values of ϵ_j^1 , $j=10,16,22,28$, as functions of optimum N . It is seen that, as predicted, full variational convergence to the number of digits given, is achieved, respectively, for $N=45(5,11)$, $109(8,17)$, $198(11,23)$, $316(14,29)$; these results were checked by comparison with the exact LPT values of Ref. 25(b), converted to our more conventional choice of units. Several additional interesting features emerge from a study of Table I. Thus, the penultimate entries in each column furnish rigorous upper bounds to the corresponding exact ϵ_j^1 ; this follows⁶⁸ because the former are computed with N values with distributions which are correct to one order lower than required in the eigenfunction, e.g., $N=273(13,27)$ yields an upper bound to the exact ϵ_{28}^1 . This special result is a consequence of a more general property of the paradigm, namely, that the distribution corresponding to any optimum N necessarily contains all orbitals required to calculate all exact lower-order results; furthermore, this feature is automatically exploited by the PV-RR formalism which selects out of the total N orbitals in each order only those that are required, commencing with $|\psi_1^1\rangle$ ($N_1=2$), then $|\psi_2^1\rangle$ ($N_0=5$, $N_2=3$), etc. Conversely, however, the distribution corresponding to any N contains a *portion* of the orbitals required to compute terms of higher order than the cutoff value of j corresponding to that N . Note that as N increases, the relative number of orbitals pertaining to still higher-order terms also increases (cf. Table I of Ref. 30); this implies that the PV-RR eigenvalue series computed with large N will not only yield the exact RS ϵ_j^1 through the cutoff value of j specified but, in addition, good to fair PV-RR approximations to the ϵ_j^1 over a considerable range of still higher orders. A good example of this effect is displayed in Table I, from which it is evident that as N increases, better and better approximations to the corresponding exact ϵ_j^1 are furnished over a wider and wider range of lower N values.

We stress that although such a simple paradigm as (26) and (27) will not, in general, be available for more complex systems, the method of analysis used in deriving it remains valid. Thus, it is far more efficient to monitor the relative importance of the contributions of the various $|\phi^l\rangle$ via the PV-RR formalism in an order-by-order manner than to attempt to judge their relative overall importance in a conventional RR calculation, as is usually done. Indeed, it would have been impossible to derive the required n, ℓ distribution of the orbitals, (26) and (27), from standard numerical diagonalization because the small perturbational effects involved are completely submerged in the total variational eigenvalues; for example, RR calculations with $N=64(6,13)$ and $N=360(15,31)$ yield ϵ_{RR}^1 values which are in *exact agreement* for $0 \leq \lambda \leq 0.010$ although correct through 13th and 31st order, respectively, in the RS eigenvalue

TABLE I. Variational convergence of hydrogenic Stark-effect PV-RR ϵ_j^1 , $j=10,16,22,28$ (in Z^2 a.u.) as functions of N .

N^a	ϵ_{10}^1	ϵ_{16}^1	ϵ_{22}^1	ϵ_{28}^1
3	-0.275×10^5	0.138×10^9	-0.880×10^{12}	0.636×10^{16}
10	-0.110×10^7	0.151×10^{12}	-0.624×10^{16}	-0.574×10^{21}
18	-0.117×10^9	-0.604×10^{15}	-0.303×10^{22}	-0.146×10^{29}
31	$-0.191 486 \times 10^9{}^b$	-0.820×10^{16}	-0.494×10^{24}	-0.303×10^{32}
45	$-0.194 531 960 466 499 \times 10^9{}^c$	-0.160×10^{17}	-0.459×10^{25}	-0.162×10^{34}
64		$-0.173 022 \times 10^{17}$	-0.101×10^{26}	-0.125×10^{35}
84		$-0.173 461 020 \times 10^{17}{}^b$	$-0.118 754 \times 10^{26}$	-0.299×10^{35}
109		$-0.173 469 704 956 31 \times 10^{17}{}^c$	$-0.120 283 354 \times 10^{26}$	$-0.382 461 \times 10^{35}$
135			$-0.120 334 204 007 \times 10^{26}$	$-0.396 301 \times 10^{35}$
166			$-0.120 335 896 029 \times 10^{26}{}^b$	$-0.397 160 185 \times 10^{35}$
198			$-0.120 335 942 041 25 \times 10^{26}{}^c$	$-0.397 188 343 \times 10^{35}$
235				$-0.397 189 549 51 \times 10^{35}$
273				$-0.397 189 603 92 \times 10^{35}{}^b$
316				$-0.397 189 605 14 \times 10^{35}{}^c$

^aThe n, ℓ distribution of the basis set for each value of N is in accordance with Eqs. (27); cf. also Table I, Ref. 30.

^bRigorous upper bound in the sense of Ref. 68.

^cVariationally converged (to the number of digits given) to the exact LPT values of Ref. 25(b); these entries remain invariant under further increase of N .

TABLE II. Stark-effect RS perturbation energy coefficients (in Z^2 a.u.) for the ground state of hydrogenic ions computed via the PV-RR formalism for various values of N .

N^a	j	$\epsilon_j^{1,b,c}$
235	24	$-0.153\,407\,588\,358 \times 10^{29}$
273	26	$-0.229\,270\,663\,418 \times 10^{32}$
316	28	$-0.397\,189\,605\,14 \times 10^{35}$
360	30	$-0.789\,781\,111\,08 \times 10^{38}$
409	32	$-0.178\,690\,818\,4 \times 10^{42}$
459	34	$-0.456\,504\,427 \times 10^{45}$
459	36	$-0.130\,786\,169 \times 10^{49}$
459	38	$-0.417\,628\,97 \times 10^{52}$
459	40	$-0.147\,820\,69 \times 10^{56}$
459	42	$-0.577\,069\,7 \times 10^{59}$
459	44	$-0.247\,343\,4 \times 10^{63}$
459	46	$-0.115\,919\,0 \times 10^{67}$
459	48	$-0.591\,760 \times 10^{70}$

^aFor $j \leq 34$, the n, ℓ distribution of the basis set is fully saturated for each value of N in accordance with Eqs. (27); for $j \geq 36$, cf. text.

^bVariationally converged to the exact LPT values of Ref. 25(b) with a maximum deviation of three units in the last digit reported.

^cSee Ref. 30 for the hydrogenic Stark effect ϵ_j^1 , $0 \leq j \leq 22$, computed via the PV-RR formalism to 18 significant digits for $N = 198(11,23)$.

series.

In our preliminary calculations,³⁰ the exact RS ϵ_j^1 , $0 \leq j \leq 22$, were computed via the PV-RR method with $N = 198(11,23)$. In the present study we have extended these PV-RR calculations to higher order with larger N . Table II presents the exact RS ϵ_j^1 , $24 \leq j \leq 48$,

computed with N up to $N = 459$; these results, verified as in Table I, have variationally converged to within a maximum deviation of three units in the last digit reported. Note that the ϵ_j^1 for $36 \leq j \leq 48$ are actually PV-RR approximations to the exact values arising from the previously discussed partial fulfillment of (26) and (27) for these higher orders for $N = 459(17,35)$; as anticipated, however, for such large N , their accuracy is quite high, yielding six significant digits in the worst case of ϵ_{48}^1 .

We have also investigated the two procedures for computing high-order polarizability components (11), namely, Eq. (28), on one hand, and Eqs. (15) and (16) on the other. Application of the two methods to the calculation of the $\alpha_{12}^{K,1}$, $\alpha_{12}^{N,1}$, and $\alpha_{12}^{F,1}$ over a wide range of N yields the results collected in Table III, which compares the variational convergence as a function of N of all components computed both ways. It is seen that in accord with theoretical predictions (cf. Sec. III D), both entries for $\alpha_{12}^{F,1}$ are identical; furthermore, the $\alpha_{12}^{K,1}$ and $\alpha_{12}^{N,1}$ computed with (16) converge variationally somewhat more rapidly than those computed with (28), the former pair, and $\alpha_{12}^{F,1}$, attaining the exact RS values at $N = 64(6,13)$ as required. By $N = 84(7,15)$, all results have variationally converged to the exact values to 14 significant digits; note that this implies that the Stark virial theorem (14) is satisfied through 12th order to this degree of accuracy at $N = 84$. In principle, $\alpha_{12}^{K,1}$ and $\alpha_{12}^{N,1}$ do not attain full variational convergence when computed with Eq. (28) until $N = 235(12,25)$; the excellent approximations for smaller N are due to the partial fulfillment of (26) and (27) in higher orders, already discussed in connection with Tables I and II.

Table IV displays the high-order RS polarizability

TABLE III. Comparison of variational convergence as a function of N of PV-RR polarizability components $\alpha_{12}^{K,1}$, $\alpha_{12}^{N,1}$, and $\alpha_{12}^{F,1}$ (all in Z^2 a.u.) for the hydrogenic Stark effect; for each value of N , the first row of entries is computed with Eq. (28) and the second with Eqs. (15) and (16).

N^a	$\alpha_{12}^{K,1}$	$\alpha_{12}^{N,1}$	$\alpha_{12}^{F,1}$
3	-1.3×10^{15}	3.7×10^{15}	-2.6×10^{15}
	-5.0×10^{15}	7.3×10^{15}	-2.6×10^{15}
10	-4.5×10^{17}	5.5×10^{17}	-1.0×10^{17}
	-2.0×10^{17}	2.9×10^{17}	-1.0×10^{17}
18	1.68×10^{20}	-2.75×10^{20}	1.16×10^{20}
	2.23×10^{20}	-3.30×10^{20}	1.16×10^{20}
31	6.288×10^{20}	-9.446×10^{20}	3.445×10^{20}
	6.603×10^{20}	-9.760×10^{20}	3.445×10^{20}
45	$7.275\,804 \times 10^{20}$	$-1.076\,026 \times 10^{21}$	$3.801\,225 \times 10^{20}$
	$7.285\,681 \times 10^{20\,b}$	$-1.077\,014 \times 10^{21\,c}$	$3.801\,225 \times 10^{20\,b}$
64	$7.300\,213\,277 \times 10^{20}$	$-1.079\,162\,433 \times 10^{21}$	$3.808\,812\,061\,884\,7 \times 10^{20\,d}$
	$7.300\,223\,118\,612\,3 \times 10^{20\,d}$	$-1.079\,163\,417\,534\,0 \times 10^{21\,d}$	$3.808\,812\,061\,884\,7 \times 10^{20\,d}$
84	$7.300\,223\,118\,612\,2 \times 10^{20\,d}$	$-1.079\,163\,417\,534\,0 \times 10^{21\,d}$	$3.808\,812\,061\,884\,6 \times 10^{21\,d}$
	$7.300\,223\,118\,612\,3 \times 10^{20\,d}$	$-1.079\,163\,417\,534\,0 \times 10^{21\,d}$	$3.808\,812\,061\,884\,6 \times 10^{21\,d}$
198	$7.300\,223\,118\,612\,3 \times 10^{20\,d}$	$-1.079\,163\,417\,534\,0 \times 10^{21\,d}$	$3.808\,812\,061\,884\,7 \times 10^{21\,d}$
	$7.300\,223\,118\,612\,3 \times 10^{20\,d}$	$-1.079\,163\,417\,534\,0 \times 10^{21\,d}$	$3.808\,812\,061\,884\,7 \times 10^{21\,d}$
235	$7.300\,223\,118\,612\,3 \times 10^{20\,d}$	$-1.079\,163\,417\,534\,0 \times 10^{21\,d}$	$3.808\,812\,061\,884\,7 \times 10^{21\,d}$
	$7.300\,223\,118\,612\,3 \times 10^{20\,d}$	$-1.079\,163\,417\,534\,0 \times 10^{21\,d}$	$3.808\,812\,061\,884\,7 \times 10^{21\,d}$

^aThe n, ℓ distribution of the basis set for each value of N is in accordance with Eqs. (27).

^bRigorous lower bound in the sense of Ref. 68.

^cRigorous upper bound in the sense of Ref. 68.

^dVariationally converged to exact RS values with a maximum deviation of one unit in the last digit reported.

TABLE IV. High-order RS polarizability components $\alpha_j^{K,1}$, $\alpha_j^{N,1}$, $\alpha_j^{F,1}$, and total polarizabilities α_j^1 (all in Z^2 a.u.) for the ground state of hydrogenic ions computed via the PV-RR formalism for $N=459$ with Eqs. (15) and (16), and uniformly rounded to five decimal places; for the $2 \leq j \leq 22$ components, see Ref. 30.

j	$\alpha_j^{K,1}$	$\alpha_j^{N,1}$	$\alpha_j^{F,1}$	α_j^1
24	44.73530×10^{52}	-66.62705×10^{52}	22.84356×10^{52}	0.95181×10^{52}
26	47.15608×10^{58}	-70.27180×10^{58}	24.04035×10^{58}	0.92463×10^{58}
28	6.66042×10^{65}	-9.93008×10^{65}	3.39076×10^{65}	0.12110×10^{65}
30	12.36001×10^{71}	-18.43527×10^{71}	6.28475×10^{71}	0.20949×10^{71}
32	29.62200×10^{77}	-44.19792×10^{77}	15.04610×10^{77}	0.47019×10^{77}
34	9.02993×10^{84}	-13.47751×10^{84}	4.58235×10^{84}	0.13478×10^{84}
36	34.54262×10^{90}	-51.57068×10^{90}	17.51457×10^{90}	0.48652×10^{90}
38	16.38220×10^{97}	-24.46409×10^{97}	8.30032×10^{97}	0.21843×10^{97}
40	9.52812×10^{104}	$-14.23188 \times 10^{104}$	4.82437×10^{104}	0.12061×10^{104}
42	67.29528×10^{110}	$-100.53752 \times 10^{110}$	34.05303×10^{110}	0.81079×10^{110}
44	57.20303×10^{117}	$-85.47579 \times 10^{117}$	28.93027×10^{117}	0.65751×10^{117}
46	58.04514×10^{124}	$-86.74878 \times 10^{124}$	29.34150×10^{124}	0.63786×10^{124}
48	69.78755×10^{131}	$-104.31402 \times 10^{131}$	35.26108×10^{131}	0.73461×10^{131}

components $\alpha_j^{K,1}$, $\alpha_j^{N,1}$, $\alpha_j^{F,1}$ computed with (15) and (16), as well as the total polarizabilities α_j^1 , all for $24 \leq j \leq 48$, and obtained via the PV-RR formalism for $N=459$; previously,³⁰ we have presented similar results for $0 \leq j \leq 22$ computed for $N=198$. The partial cancellation of the larger shifts in the components in summing via (10) to

the α_j^1 is evident. It is significant that all nonvanishing α_j^1 , and hence, all $\alpha_j^{K,1}$ and $\alpha_j^{F,1}$ are positive and all $\alpha_j^{N,1}$ are negative (cf. also Ref. 30). It follows from the definitions (11) of the components that the physical origins of the polarizabilities for the ground state of hydrogenic ions are, *in each order*, unambiguously due to a *de-*

TABLE V. PV-RR partial sums (from the $N=235$ ansatz) of Stark-effect eigenvalues for the ground state of H compared with values computed by other methods.

F (a.u.)	j_{\max}^a	$\epsilon_{\text{PV-RR}}^1$ (a.u.)	$\epsilon_{\text{other}}^1$ (a.u.)
0.001	6	-0.5000022500555518	-0.50000225005556 ^b
0.002	8	-0.5000090008890643	
0.003	10	-0.5000202545028799	
0.004	10	-0.5000360142401545	-0.5000360142400 ^b
0.005	10	-0.5000562847937930	-0.5000562847937 ^b
0.006	12	-0.5000810722190729	-0.5000810722194 ^b
0.007	12	-0.5001103839500758	-0.500110383958 ^b
0.008	14	-0.5001442288200815	-0.500144228821 ^b
0.009	16	-0.5001826170861249	-0.500182617088 ^b
0.010	16	-0.5002255604579599	-0.500225560459 ^b
0.015	26	-0.5005091201204593	
0.020	30	-0.50090922425924	-0.500909224258 ^b
0.025	24	-0.50142929180	
0.030	20	-0.5020742725	-0.5020742726071 ^c
0.040	14	-0.5037715	-0.5037715910137 ^c
0.050	10	-0.506099	-0.5061054253626 ^c
0.060	8	-0.50918	-0.509203450879 ^c
0.070	6	-0.5129	-0.51307676581 ^d
0.080	4	-0.5167	-0.51756061700 ^d
0.090	4	-0.5219	-0.52241280715 ^d
0.100	4	-0.5281	-0.52741817509 ^d
0.110	4	-0.535	-0.53245 ^e
0.120	2	-0.532	-0.53740 ^e
0.130	2	-0.538	-0.54216 ^e
0.140	2	-0.544	-0.54675 ^e
0.150	2	-0.551	-0.55120 ^e
0.200	2	-0.59	-0.57053 ^e

^aHighest order through which the PV-RR series is summed.

^bAverage of upper and lower bounds of Ref. 54.

^cReference 60; underlined digits are not physically significant.

^dReference 51(c).

^eReference 55.

crease in the average kinetic energy of the electron coupled with an increase in the average negative displacement (along the z axis) of the electron from the nucleus, these positive contributions being largely offset by the decrease in the magnitude of the average nuclear potential of the electron. This behavior is formally identical to that determined⁴³ for non-Born-Oppenheimer polarizabilities for the ground state of H_2^+ .

To demonstrate the effectiveness of conventional summation of the asymptotic RS eigenvalue series (5b) in computing the real Stark energies, we have extended the similar calculations of Ref. (24a) for the ground state of H to higher order and over a wider range of F , using the ϵ_j^1 computed with the $N=235$ ansatz. These results in ordinary a.u. are collected in Table V, where the appropriately truncated partial sums ϵ_{PV-RR}^1 are compared with the best values currently available, $\epsilon_{\text{other}}^1$, computed by nonperturbative^{51(c),54,55} and perturbative-summation⁶⁰ methods; the ϵ_{PV-RR}^1 have converged perturbationally to the exact values to within several units in the last digit reported. It is seen that in the range $0 < F \leq 0.02$ a.u., ϵ_{PV-RR}^1 is considerably more accurate than the nonperturbative results of Ref. 54. For $F \geq 0.02$ a.u., the accuracy of ϵ_{PV-RR}^1 starts to diminish, but excellent results are still obtained up to $F=0.05$ a.u., and good to fair estimates even up to $F=0.20$ a.u.

We have also computed the various energy-related Stark expectation values for the ground state of H by asymptotic summation of the RS series (7), using the appropriate $\langle \mathcal{A}_j \rangle^1$ computed with $N=235$. Table VI presents our results in ordinary a.u. for the Stark slope $(\partial \epsilon^1 / \partial F)_{PV-RR}$, obtained via the Hellmann-Feynman

TABLE VI. PV-RR partial sums (from the $N=235$ ansatz) of the eigenvalue-field slope for the ground state of H.

F (a.u.)	j_{\max}^a	$(\partial \epsilon^1 / \partial F)_{PV-RR}^b$ (a.u.)
0.001	9	$-0.450\,022\,221\,695\,298\,4 \times 10^{-2}$
0.002	11	$-0.900\,177\,844\,310\,642\,1 \times 10^{-2}$
0.003	11	$-0.135\,060\,062\,319\,652\,2 \times 10^{-1}$
0.004	13	$-0.180\,142\,502\,579\,635\,4 \times 10^{-1}$
0.005	15	$-0.225\,278\,659\,584\,522\,1 \times 10^{-1}$
0.006	17	$-0.270\,482\,232\,755\,688\,7 \times 10^{-1}$
0.007	17	$-0.315\,767\,105\,348\,130\,2 \times 10^{-1}$
0.008	21	$-0.361\,147\,385\,003\,878\,2 \times 10^{-1}$
0.009	21	$-0.406\,637\,446\,517\,107\,6 \times 10^{-1}$
0.010	23	$-0.452\,251\,977\,311\,722\,4 \times 10^{-1}$
0.015	39	$-0.682\,734\,120\,976\,70 \times 10^{-1}$
0.020	29	$-0.918\,810\,700 \times 10^{-1}$
0.025	21	-0.116 308 50
0.030	17	-0.141 920
0.035	13	-0.169 26
0.040	11	-0.199 1
0.050	7	-0.267
0.060	5	-0.34
0.070	3	-0.39
0.080	3	-0.47

^aHighest order through which the PV-RR series is summed.

^bFrom the Hellmann-Feynman theorem, Eq. (13), the slope is given by partial summation of the PV-RR series of $\langle \mathcal{H}_1 \rangle^1$; here, the even-order coefficients vanish identically.

theorem (13) by forming partial sums of the RS series of $\langle \mathcal{H}_1 \rangle^1$ over a range of F . In Table VII the asymptotically converged partial sums in a.u. of the expectation values $\langle \mathcal{T} \rangle_{PV-RR}^1$, $\langle \mathcal{V}_0 \rangle_{PV-RR}^1$, $\langle \mathcal{H}_0 \rangle_{PV-RR}^1$, and $\langle \mathcal{H}_1 \rangle_{PV-RR}^1$ are collected, as well as three independently computed values of ϵ_{PV-RR}^1 , all at $F=0.01$ a.u.; the three independent values of ϵ_{PV-RR}^1 were obtained, respectively, from Eq. (9a), from the Stark virial relationship

$$\epsilon^s = 3 \langle \mathcal{T} \rangle^s + 2 \langle \mathcal{V}_0 \rangle^s \quad (29)$$

[which follows easily from (9a) and (12)], and from Eq. (5b). All results in Tables VI and VII are judged to have converged perturbationally to the exact values to within several units in the last digit reported; there do not seem to be previous similar calculations available for comparison. Note that the range of F in Table VI is more limited than that of Table V; this follows because the RS series of $\langle \mathcal{H}_1 \rangle^1$ is more divergent [cf. (15)] than that of ϵ^1 . It is seen from Table VI that, as anticipated, the slope becomes more negative with increasing F . The exact agreement (to 16 significant digits) displayed in Table VII, among the three independent values of ϵ_{PV-RR}^1 and the conventionally computed ϵ_{RR}^1 , verifies the high degree of internal consistency of the PV-RR calculations as well as the applicability of the Stark virial theorem. Tables VI and VII demonstrate that for small F the expectation values can also be computed perturbationally with great accuracy.

In Table VIII the asymptotic convergence of the real Stark PV-RR eigenvalue series for the ground state of H is contrasted with the variational collapse⁵² of the corresponding RR calculations; since both the PV-RR and RR calculations are based on the same $N=198$ ansatz, we are in the advantageous position of being able to compare the perturbational and variational behavior of precisely the same quantities. In particular, the PV-RR eigenvalue partial sums ϵ_{PV-RR}^1 are compared with the first two RR eigenvalues ϵ_{RR}^1 and ϵ_{RR}^2 as functions of F over the range $F=0.005-0.030$ a.u. Throughout this

TABLE VII. PV-RR partial sums (from the $N=235$ ansatz) at $F=0.01$ a.u. of Stark-effect energy-related expectation values [cf. Eq. (7)] for the ground state of H.

Expectation value	PV-RR partial sum (a.u.)
$\langle \mathcal{T} \rangle_{PV-RR}^1$	0.499 321 056 503 336 5 ^a
$\langle \mathcal{V}_0 \rangle_{PV-RR}^1$	-0.999 094 364 983 984 7 ^a
$\langle \mathcal{H}_0 \rangle_{PV-RR}^1$	-0.499 773 308 480 648 2 ^a
$\langle \mathcal{H}_1 \rangle_{PV-RR}^1$	-0.452 251 977 311 722 4 $\times 10^{-1}$ ^b
ϵ_{PV-RR}^1	-0.500 225 560 457 959 9 ^c
ϵ_{PV-RR}^1	-0.500 225 560 457 959 9 ^d
ϵ_{PV-RR}^1	-0.500 225 560 457 959 9 ^e
ϵ_{RR}^1	-0.500 225 560 457 960 0 ^f

^aSummed through 20th order.

^bSummed through 23rd order.

^cSummed via Eq. (9a).

^dSummed via Stark virial equation (29).

^eSummed through 16th order via Eq. (5b).

^fComputed via numerical diagonalization of Eq. (22) for $N=235$.

TABLE VIII. The asymptotic convergence of the Stark-effect PV-RR eigenvalue series for the ground state of H contrasted with the variational collapse of corresponding RR calculations. (Both PV-RR and RR calculations are based on the $N = 198$ ansatz.)

F (a.u.)	j_{\max}^a	$-\varepsilon_{\text{PV-RR}}^1$ (a.u.)	$-\varepsilon_{\text{RR}}^1$ (a.u.)	$-\varepsilon_{\text{RR}}^2$ (a.u.)
0.005	8	0.500 056 284 793 79	0.500 056 284 793 78	0.178 111 533 470 56
0.010	12	0.500 225 560 457 96	0.500 225 560 457 95	0.348 955 478 848 96
0.014 30	20	0.500 462 468 687 02	0.500 462 468 687 00	0.498 687 518 227 24
0.014 350 0	20	0.500 465 725 399 08	0.500 465 725 399 07	0.500 436 466 844 18
0.014 350 5	20	0.500 465 758 024 83	0.500 465 758 024 82	0.500 453 957 053 78
0.014 350 8	20	0.500 465 777 600 83	0.500 465 777 600 84	0.500 464 451 186 37
0.014 350 9 ^{c,d}	20	0.500 465 784 126 26	0.500 467 949 231 76	0.500 465 784 126 23
0.014 351 0 ^d	20	0.500 465 790 651 73	0.500 471 447 277 67	0.500 465 790 651 72
0.014 352 0 ^d	20	0.500 465 855 909 03	0.500 506 427 768 30	0.500 465 855 909 02
0.014 39 ^d	20	0.500 468 339 127 68	0.501 835 728 689 12	0.500 468 339 127 67
0.020 ^e	30	0.500 909 224 259 24	0.698 801 151 164 80	0.622 747 266 457 43
0.025 ^e	24	0.501 429 291 80	0.875 170 989 819 77	0.782 836 149 215 54
0.030 ^e	20	0.502 074 272 5	1.052 013 807 182 4	0.943 384 731 718 46

^aHighest order through which the PV-RR series is summed.

^bAsymptotically converged to ε^1 .

^cThe first avoided crossing occurs at this critical value of F so that $\varepsilon_{\text{RR}}^1$ is no longer stable.

^dFor these F values, $\varepsilon_{\text{RR}}^2$ has temporarily stabilized to approximate ε^1 .

^eAdditional avoided crossings have now occurred so that $\varepsilon_{\text{RR}}^2$ is no longer stable; cf. text.

entire range, $\varepsilon_{\text{PV-RR}}^1$ is seen to converge asymptotically to the exact real energies ε^1 (cf. Table V). Furthermore, for small enough F , $\varepsilon_{\text{RR}}^1$ is stable and in excellent agreement with $\varepsilon_{\text{PV-RR}}^1$. At the critical-field strength (for $N = 198$) of $F = 0.014\,350\,9$ a.u., however, the first avoided crossing takes place abruptly (in an interval of F less than 1×10^{-7} a.u.) and one sees that $\varepsilon_{\text{RR}}^1$ has started to diverge, being replaced by the temporarily stable $\varepsilon_{\text{RR}}^2$ as the RR approximation to ε^1 . For $F = 0.020$ a.u., several avoided crossings have evidently taken place since $\varepsilon_{\text{RR}}^2$ is now diverging, and the temporarily stable RR approximation to ε^1 is furnished by $\varepsilon_{\text{RR}}^5 = -0.500\,909\,224\,259\,38$ a.u. As F continues to increase, the avoided crossings multiply and it becomes ever more difficult to locate the temporarily stable $\varepsilon_{\text{RR}}^s$ which have moved to large s . These results highlight the advantages of using the asymptotic PV-RR eigenvalue series as opposed to the RR stabilization method.

Finally, we touch upon the PV-RR calculation of the RS ground-state eigenfunction series (25b) via (25c). To illustrate in the simplest case of $|\psi_1^1\rangle$ ($N_1 = 2$), one finds via the PV-RR method for optimum $N \geq 3$ that

$$|\psi_1^1\rangle = C_{11}^{21} |210\rangle + C_{11}^{31} |310\rangle, \quad (30a)$$

where $C_{11}^{21} = -2.250\,000\,000\,000\,000 = -\frac{9}{4}$, $C_{11}^{31} = 0.559\,016\,994\,374\,947\,4 = \sqrt{5}/4$, and all other C_{11}^{j1} vanish identically or are vanishingly small; to demonstrate the accuracy of this result, note that simplification of (30a) via (20) yields

$$|\psi_1^1\rangle = \pi^{-1/2} z (1+r/2) e^{-r}, \quad (30b)$$

which is the exact solution^{6(b)}. Determination of the higher-order $|\psi_j^1\rangle$ proceeds in the same manner; in the actual calculations, of course, one uses the computer-generated decimal equivalents of the C_j^{i1} .

The PV-RR hydrogenic Stark calculations reported

herein can be readily extended to still higher order. For example, it follows from (26) and (27) that the $N = 693(21,43)$ ansatz will yield the exact RS ground-state eigenvalue series through 43rd order, and, based on our experience, supplementary good PV-RR approximations to the ε_j^1 , $j \geq 44$ through at least 60th order; this ansatz presents no difficulty since the largest ℓ block to be diagonalized³³ in \mathbf{H}_0 is only of dimensions $N_1 = 42$. Furthermore, if desired, greater accuracy in higher order can be achieved by working in quadruple precision, which is not uncommon in LOPT; this is feasible because of the simplicity and proven computational speed of PV-RR calculations in general.

V. CONCLUDING REMARKS

In the context of methodology, the present work has again demonstrated that the PV-RR formalism is capable of extracting the perturbational content of a given finite variational eigenvalue equation such as (22) to high order with great accuracy. In summary, the PV-RR formalism owes its power and flexibility to the following principal factors.

(1) Unlike the specialized methods of LOPT, the PV-RR formalism can be applied to arbitrary atomic and molecular systems because it is based upon the variational principle as well as upon perturbation theory. Moreover, the PV-RR formalism is an eminently practical procedure which can be implemented in every case where the conventional RR approach gives meaningful results, and, indeed, in certain cases where the latter breaks down, e.g., the metastable states of the Stark effect.

(2) The horribly cumbersome explicit formulations of conventional RS perturbation theory are completely avoided by the introduction of several auxiliary matrices; these lead to compact PV-RR algorithms whose recur-

sive invariant form enables the procedure to be readily programmed and facilitates the computation of the PV-RR series to large order.

(3) The PV-RR formalism automatically permits sensitive tests to be made of the degree of variational saturation resulting from the choice of the type and number of basis functions used; e.g., it was this diagnostic insight which led to the discovery of the paradigm (26) and (27).

Finally, it is of interest to compare the present PV-RR LOPT polarizability calculations for hydrogenic ions with the similar PV-RR LOPT polarizability studies⁴⁰⁻⁴³ of H_2^+ . If we arrange the systems considered in the sequence of increasing complexity, i.e., hydrogenic ions, H_2^+ within the Born-Oppenheimer approximation,⁴¹ and a non-Born-Oppenheimer model^{40,42,43} of H_2^+ , we find that the ground-state polarizability series were determined via the PV-RR formalism through 48th, 30th, and 20th order, respectively, with variational matrices of dimensions $N = 459, 576, \text{ and } 540$, where the computational effort in each case was roughly equivalent; this reduction in the maximum order computed with increasing complexity of the system is precisely in accord with expectations. It should be noted, however, that previous atomic and molecular polar-

izability calculations, using matrices of similar size as those mentioned above (or larger) and routinely based on either the variational-perturbational²⁷ or finite-perturbation⁶⁹ method, were limited to fourth-order polarizability series [see, e.g., Refs. 44, 52(c), and 70]. Thus, for a meaningful comparison with these previous low-order non-PV-RR calculations, it is appropriate to consider the computational effort expended in the PV-RR calculations to generate fairly low-order, say sixth-order, polarizability series; one finds for the sequence of systems described above that the PV-RR calculations required N values of only $N = 18, 36, \text{ and } 100$, respectively, to reach sixth order accurately. The trend of these data suggests that it should be possible to extend the PV-RR formalism to polarizability studies of more complex systems where larger variational matrices will be required.

ACKNOWLEDGMENT

One of us (J.N.S.) gratefully acknowledges the financial support given by the Cottrell Memorial Fund while at the University of Stirling.

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