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Perturbational-Variational Approach to the Calculation of Variational Wave Functions. I. Theory

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Certain aspects of Rayleigh-Schrödinger (RS) perturbation theory and of the variational principle are combined in a new perturbationally oriented variational approach for obtaining approximate solutions to Schrödinger's time-independent equation. This perturbational-variational (PV) procedure is applicable for all perturbed Hamiltonian operators which can be expanded as $H(\lambda)=\Sigma H_t\lambda^t$, where λ is an external parameter governing the strength of the perturbing terms; in particular, the theory is developed here for the important special form, $H=H_0+H_1\lambda$. It is shown how the application of the PV procedure to an arbitrary analytic approximate wave function yields the variational parameters embedded in the wave function, the wave function itself, the corresponding approximate energy, and other expectation values, all in the form of energetically optimized PV expansions in powers of λ to any desired order. A variational wave-operator formalism is introduced to deal with the multivariant expansions required to form the PV expansions. The remainder theorem and the variational Hellmann–Feynman theorem are derived and their role in the PV methodology is discussed. The principal advantages of the new method are: (1) Unlike RS perturbation theory, there is no requirement that the exact solution of a simpler unperturbed system be known; (2) the explicit λ dependence of the optimum quantities is analytically derived; (3) the numerical aspects of a given variational problem are simplified because the variational equations generated by the PV procedure are almost completely linearized in the variational parameters; and (4) the PV expansions form a natural framework for the systematic classification and evaluation of all perturbed variational wave functions in respect to their quality. The PV classification scheme, previously presented in bare outline, is rigorously derived. The insight obtained from PV theory is further illustrated by the derivation and application of the variational integral Hellmann–Feynman theorem, the virial theorem, and a theorem relating to the expectation value of the unperturbed potential. The *a priori* PV classification of perturbed variational wave functions is extended to the perturbed variational parameters embedded in the wave functions; it is shown that the anomalous PV expansions of some open-shell parameters and orbitals can be simply explained in terms of PV theory.

I. INTRODUCTION

ONE of the major problems of quantum mechanics is to develop techniques whereby approximate solutions to Schrödinger's time-independent equation

$$(H-\epsilon)\psi=0 \tag{1}$$

can be obtained and evaluated in regard to their accuracy. Here, H is the appropriate Hamiltonian operator for the system in question and ψ and ϵ are the exact, steady-state eigenfunctions and eigenvalues, respectively. In many cases of interest, H may be treated as a function of a well-defined, external perturbing parameter λ, which assumes discrete or continuous values over some range $0\leq\lambda\leq\Lambda$. In such cases, H can often be written as

$$H=H_0+H_1\lambda, \tag{2a}$$

or more generally, expanded as

$$H=H(\lambda)=\sum_{t=0}^{\infty} H_t\lambda^t, \tag{2b}$$

where

$$H_t\equiv(t!)^{-1}\left(\frac{d^tH}{d\lambda^t}\right)_{\lambda=0}. \tag{2c}$$

We are concerned here with the general problem of finding approximate solutions to Hamiltonians perturbed in this manner; an important example is furnished by atomic isoelectronic sequences, for which,

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via a transformation to modified atomic units[1] due to Hylleraas,[2] the nonrelativistic Hamiltonian can be cast in the form of Eq. (2a), where $\lambda = Z^{-1}$.

As is well known, two principal methods of obtaining approximate solutions to Eq. (1) are based on (1) the variational principle, and (2) Rayleigh-Schrödinger (RS) perturbation theory or some variant thereof. In the present work, the first paper of a series, it is shown how some of the difficulties associated with the conventional variational approach and with RS perturbation theory can be avoided by combining certain aspects of these methods in a new perturbationally oriented variational procedure. This analytic perturbational-variational (PV) procedure is contrasted with the standard methods in Sec. IIA, and the methodology of the new procedure is derived in Secs. IIB–IID and in Appendices A–C.

In essence, the application of the PV procedure to an arbitrary, analytic approximate wave function yields the variational parameters embedded in the wave function; the wave function itself; and the corresponding approximate energy and other expectation values; all in the form of energetically optimized expansions in powers of the perturbing parameter λ. Thus, the PV procedure provides variational data for a given perturbed system as a function of the perturbation. Of greater interest than any specific numerical results, however, is the fact that the PV expansions, in conjunction with associated theorems derived in Appendices D–G, serve as a powerful diagnostic tool for investigating and predicting the relative accuracy of different categories of variational wave functions.[3] This interpretive aspect of the PV procedure is discussed and illustrated in Sec. III. Finally, in Sec. IV, the method is summarized and some suitable future applications are suggested.

The PV procedure developed here is general in scope and applicable to all approximate wave functions for which the optimum expansions exist; further, the expansions can be computed to any desired order in a computationally simple manner. In previous related work, Scherr and Silverman[4] have determined the first two or three expansion orders of the variational parameters and of several expectation values for a number of variational wave functions for the helium isoelectronic sequence by a limiting algebraic procedure, and Machacek and Scherr[5] have made similar calculations for the lithium sequence. These calculations are of a specialized nature, involving several simplifying assumptions dependent upon the form of the wave function; further, their approach does not permit a clear-cut separation of the various expansion orders and is difficult to extend to higher orders because it involves the solution of algebraic equations of successively higher degree. A simple numerical differencing procedure, originally developed by Scherr, Silverman, and Matsen[6] for application to experimental energies, is also available for recovering the leading terms of the expansions of optimum variational parameters and expectation values. This numerical method has been applied to variational data for atomic isoelectronic sequences by Scherr and Silverman[7] and by Silverman and Brigman.[3] Although a valuable supplementary technique, the numerical procedure is restricted in application because it requires accurate variational results as input data, computed by standard variational means for several adjacent values of λ; in addition, this technique is limited to the accurate determination of the first few expansion terms due to the successive accumulation of error with increasing order.[6]

II. THE PV PROCEDURE

A. Comparison with Standard Methods

The PV procedure represents a new, analytically oriented approach to the task of optimizing a given approximate wave function via the energy criterion for a system with a Hamiltonian described by Eqs. (2). The details of the procedure are developed in the following subsections; in this subsection the general aspects of the PV procedure are compared with those of the standard variational method and of RS perturbation theory to illustrate their respective points of difference and of similarity.

Consider an arbitrary, analytic, normalized approximation, φ, to ψ for a given state of the system under consideration. In general, φ which is taken to be constructed with the proper symmetry, may contain P adjustable parameters, the a_μ; thus,

$$\varphi = \varphi(a_1, a_2, \cdots, a_P) \equiv \varphi\{a_\mu\}, \tag{3}$$

where the a_μ may occur linearly, nonlinearly, or in some combination. It should be noted that the form of φ considered in Eq. (3) and throughout has no explicit dependence on λ; any λ dependency is introduced implicitly through the a_μ. The normalization of φ can always be arranged so as to be independent of the specific values assigned to the a_μ. Then, for arbitrary values of the a_μ,

$$S \equiv \langle \varphi\{a_\mu\} | \varphi\{a_\mu\} \rangle = 1, \tag{4}$$

and from the variational principle,[8] for H given by

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[1] The modified atomic units of energy and length may be obtained from the usual Hartree atomic units by replacing the electronic charge e with $eZ^{1/2}$, where Z is the nuclear charge; see H. Shull and G. G. Hall, Nature **184**, 1559 (1959).

[2] E. A. Hylleraas, Z. Physik **65**, 209 (1930); E. A. Hylleraas and J. Midtdal, Phys. Rev. **103**, 829 (1956); **109**, 1013 (1958).

[3] See J. N. Silverman and G. H. Brigman [Rev. Mod. Phys. **39**, 228 (1967)] for such a diagnostic application of PV expansions to variational wave functions for atomic isoelectronic sequences.

[4] C. W. Scherr and J. N. Silverman, J. Chem. Phys. **32**, 1407 (1960).

[5] M. Machacek and C. W. Scherr, J. Chem. Phys. **33**, 242 (1960).

[6] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).

[7] C. W. Scherr and J. N. Silverman, J. Chem. Phys. **37**, 1154 (1962).

Eqs. (2),

$$\epsilon \leq \eta\{a_\mu;\lambda\} \equiv \langle \varphi\{a_\mu\} | H(\lambda) | \varphi\{a_\mu\} \rangle, \qquad (5)$$

where the approximate energy η is an upper bound to ϵ. Further, for an arbitrary operator A independent of λ, the expectation value is given by

$$\langle A \rangle = \langle A\{a_\mu\} \rangle \equiv \langle \varphi\{a_\mu\} | A | \varphi\{a_\mu\} \rangle. \qquad (6)$$

In the standard variational approach,[9] the best upper bound to ϵ for the chosen form of φ is sought by variation of the a_μ, yielding the set of variational equations

$$\frac{\partial \eta}{\partial a_\mu} = \left\langle \frac{\partial \varphi}{\partial a_\mu} \middle| H(\lambda) \middle| \varphi \right\rangle + \left\langle \varphi \middle| H(\lambda) \middle| \frac{\partial \varphi}{\partial a_\mu} \right\rangle = 0; \qquad (7)$$

$$\mu = 1,2,\cdots,P.$$

Ideally, one would solve Eqs. (7) analytically so as to obtain the optimum[10] parameters, the $\bar{a}_\mu$, which are necessarily explicit functions of λ,

$$\bar{a}_\mu = \bar{a}_\mu(\lambda); \quad \mu = 1,2,\cdots,P. \qquad (8a)$$

Correspondingly, the energetically optimized[10] quantities, the wave function $\bar{\varphi}$, the energy $\bar{\eta}$, and the expectation value $\langle \bar{A} \rangle$, would then be explicitly given as functions of λ,

$$\bar{\varphi} = \varphi\{\bar{a}_\mu(\lambda)\}, \qquad (8b)$$

$$\bar{\eta} = \eta\{\bar{a}_\mu(\lambda);\lambda\} = \langle \bar{\varphi} | H(\lambda) | \bar{\varphi} \rangle, \qquad (8c)$$

$$\langle \bar{A} \rangle = \langle A\{\bar{a}_\mu(\lambda)\} \rangle = \langle \bar{\varphi} | A | \bar{\varphi} \rangle; \qquad (8d)$$

thus, for a given approximate wave function, one variational calculation would in principle suffice for the entire range of λ. In all but the simplest cases, however, it is usually impossible or impracticable to solve Eqs. (7) for the $\bar{a}_\mu$ in closed form. Normally, one must be content with different numerical solutions for specific values of λ, obtained by iterative techniques requiring large-scale computers. Therefore, the optimized results usually consist of a large collection of numerical data in tabulated form for various values of λ in the range of interest. The disadvantages of this approach may be summarized as follows:

(1) The loss of the explicit λ dependency necessitates a new calculation for each value of λ with concomitant loss of compactness.

(2) An electronic computer is required for even relatively simple variational wave functions.

(3) It is well known[11] that the optimized energy is insensitive to small variations in the optimum variational parameters; conversely, in the standard numerical approach, the optimum energy is a poor criterion for refining variational parameters to a high degree of accuracy. Thus, other expectation values, which are in general more sensitive to the variational parameters, cannot be obtained as accurately as the energy.

(4) A more fundamental objection to the conventional variational procedure arises from its inability to give either *a priori* guidance in the selection of approximate wave functions or *a posteriori* insight into the superiority of one type of approximate solution over another; in this connection, for Hamiltonians of the form of Eqs. (2), the relative order of energetic superiority of a group of different approximate wave functions may be a function of λ, but the variational principle, taken alone, offers no explanation.

In the PV procedure, both the manner of derivation and the form of presentation of the energetically optimized results differ significantly from those of the standard variational method. The optimum quantities, Eqs. (8), are analytically obtained in the form of the Taylor expansions about $\lambda = 0$:

$$\bar{a}_\mu = \sum_{j=0}^{\infty} \bar{a}_{\mu j} \lambda^j; \quad \mu = 1,2,\cdots,P, \qquad (9a)$$

$$\bar{\varphi} = \sum_{r=0}^{\infty} \bar{\varphi}_r \lambda^r, \qquad (9b)$$

$$\bar{\eta} = \sum_{m=0}^{\infty} \bar{\eta}_m \lambda^m, \qquad (9c)$$

and

$$\langle \bar{A} \rangle = \sum_{m=0}^{\infty} \langle \bar{A} \rangle_m \lambda^m. \qquad (9d)$$

Of course, if the explicit optimum functional relationships of Eqs. (8) could be analytically determined, it would be straightforward to obtain the PV expansions of Eqs. (9). In the PV procedure, however, the reverse approach is employed, i.e., the expansions are first obtained in *unoptimized* form and then optimized order by order to build up the optimum functions to any desired order. This technique circumvents some of the previously mentioned inherent difficulties of the conventional method in the following manner:

(1) The explicit λ dependency of the optimum quantities is analytically derived.

(2) The computational aspects of a given variational problem are greatly simplified because the variational equations generated by the PV procedure are almost completely linearized in the variational parameters;

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[8] It is assumed throughout that the variational principle is applicable. Moreover, in case the variational principle exists for functionals other than the energy (such as the statistical variance) and is used as a basis for obtaining approximate solutions, the main theoretical results of the PV procedure remain applicable; see Ref. 14 for formal details.

[9] See, for example, B. L. Moiseiwitsch, *Quantum Theory I, Elements*, edited by D. R. Bates (Academic Press Inc., New York, 1961), pp. 211–228.

[10] In this notation, the use of a superior bar denotes an energetically optimized quantity; the omission of the bar denotes an unoptimized quantity with an arbitrarily assigned value.

[11] See, for example, H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957), p. 164.

as a consequence, the use of a desk computer is feasible in many calculations.[12]

(3) The order-by-order optimization of the energy and the linear structure of the variational equations enable the optimum variational parameters, corresponding to the chosen form of the variational wave function, to be determined to any desired degree of accuracy.

(4) A number of important theoretical relationships (dealt with in Sec. III, Appendices B–G, and elsewhere[12–14]) applicable to arbitrary, optimized variational wave functions, energies, and other expectation values, emerge in transparent form as a general by-product of the PV procedure; these relationships, which are concealed or obscured in the conventional numerical approach, give considerable guidance in the selection of and insight into the relative behavior of different types of variational wave functions.

The points of departure for RS perturbation theory[15] are the known zero-order solutions ψ_0 and ϵ_0 of the unperturbed Schrödinger equation

$$(H_0-\epsilon_0)\psi_0=0. \tag{10}$$

The exact perturbed solutions ψ and ϵ are then considered as functions of λ which can be expanded in Taylor series about $\lambda=0$:

$$\psi=\psi(\lambda)=\sum_{r=0}^{\infty}\psi_r\lambda^r, \tag{11a}$$

and

$$\epsilon=\epsilon(\lambda)=\sum_{m=0}^{\infty}\epsilon_m\lambda^m. \tag{11b}$$

The substitution of Eqs. (11) in Eq. (1) yields an infinite set of coupled differential equations of which Eq. (10) is the first one; in principle, the successive solution of these equations, order by order, would yield the successive terms of the ψ and ϵ expansions, but, in practice, this is seldom possible. To overcome this difficulty, a variational-perturbation procedure, originally developed by Hylleraas[2] and generalized by Knight and Scherr,[16] has been devised for the variational calculation of the ψ_r and ϵ_m to any desired order. The validity of this variational procedure for a given higher order depends upon the implicit assumption that all lower orders of the ψ_r and ϵ_m required in the calculation have been accurately approximated; this becomes increasingly difficult to accomplish with increasing complexity of the system considered.

The PV expansions, Eqs. (9), bear a formal analogy to the RS expansions, Eqs. (11). Indeed, as is shown in Appendices B–F, there are a number of theorems which apply in an identical or similar manner to the expansions both of optimized approximate quantities and of the exact quantities. It should be carefully noted that despite these points of similarity, the PV procedure differs both in objectives and in methods from RS perturbation theory and from the Hylleraas-Knight-Scherr variational-perturbation procedure. Thus, in the PV procedure, there is no requirement that ψ_0 and ϵ_0 be known, or equivalently, that $\bar{\varphi}_0$ and $\bar{\eta}_0$ satisfy Eq. (10); similarly, there is no requirement that the solutions be known for the higher-order differential equations of RS perturbation theory. Further, in RS perturbation theory, the ψ_r and ϵ_m are defined as Taylor coefficients, but no direct use of this can be made since $\psi(\lambda)$ and $\epsilon(\lambda)$ are not known; in the PV procedure, to the contrary, the identification of the φ_r and η_m as Taylor coefficients plays an essential role in determining these expansions. In the limit of increasing accuracy, both methods should yield identical results; in general, however, the $\bar{\varphi}$ and $\bar{\eta}$ expansions, Eqs. (9b) and (9c), derived from the optimization of an arbitrary φ, would not agree term by term with the corresponding ψ and ϵ expansions, Eqs. (11a) and (11b). Such comparisons of the expansions of optimized approximate quantities and of exact quantities prove to be of great utility and are discussed in Sec. III.

B. The Expansion and Optimization Technique

We restrict ourselves here to the important special case of H given by Eq. (2a), as this is sufficient to establish all the essential details of the procedure; the generalization to H of Eq. (2b) as well as some aspects of the convergence of PV expansions are considered elsewhere.[14] Then Eq. (5) for the unoptimized energy can be written in the form

$$\eta=G\{a_\mu\}+g\{a_\mu\}\lambda, \tag{12}$$

where

$$G\{a_\mu\}\equiv\langle\varphi\{a_\mu\}|H_0|\varphi\{a_\mu\}\rangle, \tag{13a}$$

and

$$g\{a_\mu\}\equiv\langle\varphi\{a_\mu\}|H_1|\varphi\{a_\mu\}\rangle. \tag{13b}$$

The desired optimum solutions for the parameters, Eqs. (8a), suggest that we regard the unoptimized a_μ as arbitrary analytic functions of λ which can be expanded in Taylor series about $\lambda=0$:

$$a_\mu=a_\mu(\lambda)=\sum_{j=0}^{\infty}a_{\mu j}\lambda^j;\quad \mu=1,2,\cdots,P. \tag{14}$$

It follows from Eqs. (14) that the unoptimized func-

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[12] J. N. Silverman and J. C. van Leuven (to be published). These calculations illustrate the application of the PV computational procedure to several variational wave functions for the He isoelectronic sequence.

[13] J. N. Silverman (to be published).

[14] J. C. van Leuven and J. N. Silverman (to be published); this study presents a more mathematically oriented, generalized treatment of the theory of the PV procedure.

[15] See, for example, A. Dalgarno, *Quantum Theory I, Elements*, edited by D. R. Bates (Academic Press Inc., New York, 1961), pp. 171–209

[16] R. E. Knight and C. W. Scherr, J. Chem. Phys. **37**, 2503 (1962); Phys. Rev. **128**, 2675 (1962); Rev. Mod. Phys. **35**, 431 (1963); C. W. Scherr and R. E. Knight, *ibid.* **35**, 436 (1963).

tionals, φ, G, g, and $\langle A\rangle$, can be expanded analogously:

$$X=\sum_{m=0}^{\infty} X_m\lambda^m, \tag{15a}$$

where

$$X=\varphi,\, G,\, g,\, \langle A\rangle. \tag{15b}$$

By equating coefficients of like powers of λ, we obtain the following formal results for the energy expansion from Eqs. (12) and (15):

$$\eta_0=G_0, \tag{16a}$$

and

$$\eta_m=G_m+g_{m-1},\quad m\geq 1. \tag{16b}$$

In addition to being defined as Taylor coefficients of integral functionals, the G_m, g_m, and $\langle A\rangle_m$ are also defined in terms of matrix elements over expansion terms of φ. Thus, for example, it follows from Eqs. (13a) and (15) that

$$G_m=\sum_{r=0}^{m} \langle \varphi_r|H_0|\varphi_{m-r}\rangle, \tag{17}$$

with analogous expressions for g_m and $\langle A\rangle_m$. Similarly, the expansion orthonormality conditions are obtained from Eq. (4):

$$S_0=\langle\varphi_0|\varphi_0\rangle=1, \tag{18a}$$

and

$$S_m=\sum_{r=0}^{m} \langle\varphi_r|\varphi_{m-r}\rangle=0,\quad m\geq 1. \tag{18b}$$

Since the X of Eqs. (15) are all implicit functions of λ through the a_μ, additional analysis, which is presented in Appendix A, is required to obtain the explicit form of the X_m. In terms of the operators d_j and $W_{m,m}$, defined in Appendix A, the expansion terms of the X are given by

$$X_0=X\{a_{\mu 0}\}, \tag{19a}$$

$$X_1=d_1X_0, \tag{19b}$$

$$X_2=\left(d_2+\frac{d_1^2}{2!}\right)X_0, \tag{19c}$$

$$X_3=\left(d_3+d_1d_2+\frac{d_1^3}{3!}\right)X_0, \tag{19d}$$

and in general, by

$$X_m=W_{m,m}X_0,\quad m\geq 0. \tag{19e}$$

We have explicitly written down the first few terms in the expansion of the X to illustrate the effects of the constraints [see Eqs. (A13) and Table II, Appendix A] on the $W_{m,m}$ operator. The analysis in Appendix A shows that as a result of these constraints, X_m is in general a function of all $a_{\mu j}$ for $0\leq j\leq m$, and for $m\geq 1$, the highest-order parameters, the $a_{\mu m}$, occur *linearly* in X_m; this almost complete linearization of the variational parameter expansions, order by order, is essential to the PV optimization procedure.

It is important to note the distinction between the application of $W_{m,m}$ to integral functionals such as G_0, g_0, $\langle A\rangle_0$, and S_0, on one hand, and to φ_0, on the other hand. For example,

$$G_m=W_{m,m}G_0=W_{m,m}\langle\varphi_0|H_0|\varphi_0\rangle, \tag{20a}$$

but in terms of matrix elements over φ_r, it follows from Eq. (A20) of Appendix A that

$$G_m=\sum_{r=0}^{m} \langle W_{r,r}\varphi_0|H_0|W_{m-r,m-r}\varphi_0\rangle, \tag{20b}$$

with analogous expressions for g_m, $\langle A\rangle_m$, and S_m; Eq. (20b) can also be directly derived from Eqs. (17) and (19e).

From Eqs. (16) and (19), we obtain the general result

$$\eta_m=W_{m,m}G_0+W_{m-1,m-1}g_0,\quad m\geq 0, \tag{21}$$

where in accordance with our conventions (see Appendix A), $W_{m-1,m-1}g_0=0$ for the special case of $m=0$. We may now regard η as a function of all the expansion orders of the a_μ,

$$\eta=\eta\{a_{\mu 0},a_{\mu 1},\cdots,a_{\mu m},\cdots;\lambda\}, \tag{22}$$

where the $a_{\mu j}$ are to be variationally determined. Then, it follows from Eqs. (12), (15), and (22) that the conditions for determining the optimum zero-order parameters, the $\bar{a}_{\mu 0}$,

$$\frac{\partial\eta}{\partial a_{\mu 0}}\equiv D_{\mu 0}\eta=0;\quad \mu=1,2,\cdots,P, \tag{23}$$

lead to the equivalent set of conditions

$$D_{\mu 0}\eta_m=0;\quad \mu=1,2,\cdots,P;\quad 0\leq m\leq\infty. \tag{24}$$

It is easy to show that the conditions of Eqs. (24) are sufficient to determine all expansion orders of the optimum $\bar{a}_{\mu j}$, order by order, and that no new conditions are obtained by partial differentiation of the η_m in respect to $a_{\mu j}$ for $j\geq 1$. Thus, for $m=0$,the conditions

$$D_{\mu 0}\eta_0=D_{\mu 0}G_0=0;\quad \mu=1,2,\cdots,P \tag{25a}$$

yield P simultaneous equations involving only the $a_{\mu 0}$. In the general case, this zero-order set of variational equations is nonlinear in the $a_{\mu 0}$ and may have to be solved for the optimum $\bar{a}_{\mu 0}$ by some iterative technique; in the special case where all a_μ occur in φ linearly, as in the Rayleigh-Ritz type of variational wave function, the zero-order equations can be obtained in linear, homogeneous form and solved in the usual manner via the secular determinant. For all types of parameters, however, the solution of Eqs. (25a) in the PV procedure would be simpler than the solution of Eqs. (7) encountered in the standard variational approach because only the simpler operator H_0 is involved in the former rather than the total H and there is no λ dependency to take into account; in addition, as is discussed in Sec. III, the optimum $\bar{a}_{\mu0}$ may be known in some cases from theory.

After the $\bar{a}_{\mu0}$ have been determined, the optimum conditions for $m=1$,

$$D_{\mu0}\eta_1=0;\quad \mu=1,2,\cdots,P, \tag{25b}$$

yield P simultaneous linear inhomogeneous equations in the $a_{\mu1}$, involving in addition only the known $\bar{a}_{\mu0}$. The optimum $\bar{a}_{\mu1}$ are then determined by solving these first-order variational equations by standard linear means. On the other hand, the alternate optimum conditions obtained by partial differentiation of η_1 in respect to the $a_{\mu1}$,

$$\partial\eta_1/\partial a_{\mu1}=0;\quad \mu=1,2,\cdots,P, \tag{25b$'$}$$

merely lead again to the zero-order equations for the $a_{\mu0}$, Eqs. (25a), as may be seen from Eq. (A8) of Appendix A, and Eqs. (19a), (19b), and (21). After the $\bar{a}_{\mu1}$ have been determined from Eqs. (25b), the process is extended to the determination of the $\bar{a}_{\mu2}$ with the second-order variational equations obtained from the conditions $D_{\mu0}\eta_2=0$, etc. For each order of $m\geq1$, P simultaneous linear inhomogeneous variational equations in the $a_{\mu m}$ are obtained, containing in addition only the known lower orders of the $\bar{a}_{\mu j}$, $0\leq j<m$. These calculations can be extended in this manner to any desired order.

The integral functional and the matrix-element formulations presented above are entirely equivalent and lead to identical results. Essentially, the former procedure requires initial integration with subsequent differentiation, while the latter procedure reverses the order of these operations. Usually, the calculation of expectation values is simpler in the integral functional approach while, if interest is focussed on the behavior of the wave function, greater theoretical insight is obtained with the matrix-element approach. In the subsequent discussion, we use either or both formulations interchangeably, depending on which aspects of the PV procedure are to be emphasized.

All of the equations in this subsection apply to optimized as well as unoptimized approximate functions, and indeed, to the exact quantities as well. Therefore, Eqs. (14)–(21) may be termed the *general* expansions of the PV procedure. By appropriate substitution of the optimum $\bar{a}_{\mu j}$, $0\leq j\leq m$, in Eqs. (19)–(21), the optimum[17] $\bar{d}_j$, $\bar{W}_{m,m}$, $\bar{X}_m$, and $\bar{\eta}_m$ can all be obtained through the highest order of the $\bar{a}_{\mu j}$ computed. It would thus appear that a knowledge of the optimum $\bar{a}_\mu$ expansions through the mth order is required to evaluate the optimum $\bar{X}$ and $\bar{\eta}$ expansions through the mth order; alternatively, in the matrix-element formulation, it would appear that a knowledge of the optimum $\bar{\varphi}$ expansion through the mth order is required to determine the $\bar{X}$ and $\bar{\eta}$ expansions through like order. For the optimized quantized quantities, however, it is possible to effect certain systematic reductions in the order of the $\bar{a}_{\mu j}$ and of the $\bar{\varphi}_r$ required to compute the $\bar{\eta}$ expansion to a given order; these reductions are discussed in the following subsection.

C. The Energetic Reductions in Parametric Order

Two essentially different methods are available for obtaining the optimum $\bar{\eta}$ expansion to orders higher than the highest order computed of the optimum $\bar{a}_\mu$ expansions. These methods are based respectively on the remainder theorem, derived in Appendix B, and on the variational Hellmann-Feynman theorem, derived in Appendix C.

From Eqs. (B10), Appendix B, the remainder theorem assumes the following form in the functional representation:

$$\bar{\eta}_0=\bar{G}_0, \tag{26a}$$

$$\bar{\eta}_1=\bar{g}_0, \tag{26b}$$

$$\bar{\eta}_2=(\bar{d}_1{}^2/2!)G_0+\bar{d}_1g_0, \tag{26c}$$

$$\bar{\eta}_3=(\bar{d}_1{}^3/3!)G_0+(\bar{d}_1{}^2/2!)g_0, \tag{26d}$$

and in general, for $n\geq0$,

$$\bar{\eta}_{2n}=\bar{W}_{2n,n}G_0+\bar{W}_{2n-1,n}g_0, \tag{26e}$$

and

$$\bar{\eta}_{2n+1}=\bar{W}_{2n+1,n}G_0+\bar{W}_{2n,n}g_0. \tag{26f}$$

Here, we have explicitly written down the first few terms of the $\bar{\eta}$ expansion to illustrate the effects of the constraints [see Eqs. (A14), Appendix A] on the asymmetric $W_{m,n}$ operator. It follows directly from the definition of $W_{m,n}$ and from Eqs. (26) that the optimum $\bar{a}_\mu$ expansions through nth order suffice to compute the optimum $\bar{\eta}$ expansion through $(2n+1)$th order; this result may be regarded as the quantitative formulation of the previously mentioned qualitative observation that variationally optimized energies are insensitive to small changes in the variational parameters. The remainder theorem is in striking analogy to the well-known theorem[15] from RS perturbation theory, which states that the ψ expansion through nth order suffices to compute the ϵ expansion through $(2n+1)$th order [see Eqs. (11)]. The analogy is not complete, however, as may best be seen from the matrix-element formulation of the remainder theorem, obtained by a straightforward application of Eqs. (A21), Appendix A, to Eqs. (26). This shows that the computation of $\bar{\eta}_{2n+1}$ requires not only the $\bar{\varphi}$ expansion through nth order but, in addition, a portion of each $\bar{\varphi}_s$ for $n+1\leq s\leq 2n+1$; these incomplete $\bar{\varphi}_s$, given by $\bar{W}_{s,n}\varphi_0$, may be simply described as the remainder functions obtained by the systematic omission of all terms containing $\bar{a}_{\mu j}$ for $j>n$ from the complete $\bar{\varphi}_s$. Alternately, the asymmetric $W_{m,n}$ operator may be obtained from the symmetric

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[17] The use of the superior bar in the operators $\bar{d}_j$, $\bar{W}_{m,m}$, etc., indicates that all derivatives have been evaluated at the optimum $\bar{a}_{\mu0}$, and that the optimum values of the othes $\bar{a}_{\mu j}$ involved have been appropriately substituted; see Ref. 10.

$W_{m,m}$ operator by systematically omitting all terms containing $\bar{d}_j$ for $j>n$, as is illustrated in Eqs. (26). Finally, the remainder theorem assumes its most restricted form in Eq. (B11), Appendix B, which enables the optimum $\bar{G}$ to be computed through the $(m+1)$th order from the optimum $\bar{a}_\mu$ expansions through the mth order.

Alternate expansions for the optimum $\bar{\eta}$ are derived from the variational Hellmann-Feynman theorem. From Eq. (C4), Appendix C, and Eqs. (17) and (19), we obtain

$$\bar{\eta}_1=\bar{g}_0=\langle\bar{\varphi}_0|H_1|\bar{\varphi}_0\rangle, \tag{27a}$$

$$\bar{\eta}_2=\tfrac{1}{2}\bar{d}_1 g_0=\langle\bar{\varphi}_0|H_1|\bar{\varphi}_1\rangle, \tag{27b}$$

$$\begin{aligned}\bar{\eta}_3&=\tfrac{1}{3}[\bar{d}_2+(\bar{d}_1{}^2/2!)]g_0\\&=\tfrac{1}{3}[2\langle\bar{\varphi}_0|H_1|\bar{\varphi}_2\rangle+\langle\bar{\varphi}_1|H_1|\bar{\varphi}_1\rangle],\end{aligned} \tag{27c}$$

and in general, for $m\geq 0$,

$$\begin{aligned}\bar{\eta}_{m+1}&=(m+1)^{-1}\bar{\bar{W}}_{m,m}g_0\\&=(m+1)^{-1}\sum_{r=0}^{m}\langle\bar{\varphi}_r|H_1|\bar{\varphi}_{m-r}\rangle;\end{aligned} \tag{27d}$$

the matrix-element terms in Eqs. (27b) and (27c) have been simplified by making use of the Hermitian character of H_1 and by assuming, for convenience, but without loss of generality,[18] that the $\bar{\varphi}_r$ are real. Equivalently, from Eqs. (C6) and (C7), Appendix C, we obtain

$$\bar{\eta}_0=\bar{G}_0, \tag{28a}$$

$$\bar{\eta}_2=-(\bar{d}_1{}^2/2!)G_0, \tag{28b}$$

$$\bar{\eta}_3=-\tfrac{1}{2}[\bar{d}_1\bar{d}_2+(\bar{d}_1{}^3/3!)]G_0, \tag{28c}$$

and in general, for $m\geq 1$,

$$\bar{\eta}_{m+1}=-m^{-1}\bar{\bar{W}}_{m+1,m}G_0. \tag{28d}$$

It is seen from Eqs. (27) or (28) that this approach yields the optimum $\bar{\eta}$ expansion to only one order higher than the corresponding optimum $\bar{a}_\mu$ expansions. Although the variational Hellmann-Feynman theorem is not as powerful as the remainder theorem in respect to reduction of parametric order, the former theorem does have the advantage of yielding a clear-cut separation of the unperturbed and perturbing contributions to the optimum energy. Thus, from Eqs. (27), all orders of $\bar{\eta}$, excepting $\bar{\eta}_0$, can be computed solely in terms of H_1, and from Eqs. (28), all orders of $\bar{\eta}$,excepting $\bar{\eta}_1$, can be computed solely in terms of H_0; this separation cannot be achieved with the remainder theorem, Eqs. (26). Equation (27a) offers the theoretical justification for the often-used empirical technique of computing the first-order correction to a variationally obtained zero-order energy in this manner.[19] It is interesting to note from Eq. (C5), Appendix C, that the unperturbed and perturbing contributions to the $\bar{\eta}_m$ tend to cancel increasingly with increasing order m in analogy with the like behavior of the exact quantities.[20]

The reductions in parametric order obtained with the remainder and the variational Hellmann-Feynman theorems are direct consequences both of the λ dependency of H and of the variational determination of $\bar{\eta}$. In general, therefore, the energetically optimized expectation values of other operators do not satisfy these theorems; the computation of such expectation values through mth order must be done without any reduction in parametric order using the symmetric $W_{m,m}$ operator as in the general expansions of Eqs. (19) and (20).

D. The Cyclic Flow of PV Calculations

The unoptimized input data in all PV calculations consist of φ_0, G_0, g_0, and the $\langle A\rangle_0$ for the properties of interest, all of which are obtained in analytic form from the chosen φ. It follows from the structure of the symmetric $W_{m,m}$ operator, Appendix A, that the successive higher-order terms of the expansions of the unoptimized φ, G, g, and η, can be analytically constructed by suitable weighting and grouping of the expressions for the partial derivatives formed during optimization of the lower orders of η via Eqs. (24). Thus, the formation of the $D_{\mu 0}\eta_0$ in Eqs. (25a) generates the terms required for G_1, which, together with g_0, yields η_1 via Eq. (16b) or (21); similarly, the formation of the $D_{\mu 0}\eta_1$ yields the additional terms required to derive G_2, g_1, and hence η_2, etc. Therefore, the PV calculations assume a naturally cyclic character which is schematically outlined in Table I. During a routine cycle, the $(n+1)$th, for example, η_n is formed and differentiated to yield the nth-order variational equations; these equations are solved for the $\bar{a}_{\mu n}$, which together with the previously determined lower-order $\bar{a}_{\mu j}$, suffice to compute $\bar{\varphi}_n$, $\bar{G}_{n+1}$ [via Eq. (B11)], $\bar{g}_n$, $\bar{\eta}_{n+1}$, and $\langle\bar{A}\rangle_n$, to conclude the cycle. In such a routine cycle, the energy is most readily computed via Eqs. (16), (27), or (28), as the required optimum expressions for these equations are all generated during the cycle; these three alternate formulations afford a useful check on the energy calculations. After sufficient orders have been computed to attain the desired degree of convergence,[21] the cycling process is terminated, and the remainder theorem is then employed; thus, if the last cycle were the $(n+1)$th, the n-fold application of the remainder theorem, Eqs. (26),

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[18] See, for example, E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1957), p. 33; see also S. T. Epstein, Am. J. Phys. **22**, 613 (1954).

[19] The validity of Eq. (27a) for $\bar{\eta}_1$ depends upon the fact that $\bar{G}_1=\langle\bar{\varphi}_0|H_0|\bar{\varphi}_1\rangle+\langle\bar{\varphi}_1|H_0|\bar{\varphi}_0\rangle$ vanishes; in general, this is true only for exact functions because of Eqs. (10) and (18), or for variationally optimized functions because of Eq. (C5).

[20] W. J. Carr, Jr., Phys. Rev. **106**, 414 (1957); see also Ref. 27.

[21] See Ref. 12 for a discussion of the different degrees of convergence of several variational wave functions for the He isoelectronic sequence; see also Ref. 14 for a more general discussion of convergence.

TABLE I. Cyclic flow sheet of PV calculations.

Cycle	Unoptimized quantities generated during previous cycle	Variational equations	Optimized quantities computed at end of cycle
1	$\varphi_0,G_0,g_0,\eta_0(=G_0),\langle A\rangle_0$	$D_{\mu0}\eta_0=0$	$\bar{a}_{\mu0},\bar{\varphi}_0,\bar{G}_0,\bar{g}_0,\bar{\eta}_0(=\bar{G}_0),\bar{\eta}_1(=\bar{g}_0),\langle\bar{A}\rangle_0$
2	$\varphi_1,G_1,\eta_1,\langle A\rangle_1$	$D_{\mu0}\eta_1=0$	$\bar{a}_{\mu1},\bar{\varphi}_1,\bar{G}_2,\bar{g}_1,\bar{\eta}_2,\langle\bar{A}\rangle_1$
3	$\varphi_2,G_2,g_1,\eta_2,\langle A\rangle_2$	$D_{\mu0}\eta_2=0$	$\bar{a}_{\mu2},\bar{\varphi}_2,\bar{G}_3,\bar{g}_2,\bar{\eta}_3,\langle\bar{A}\rangle_2$
$n+1$ [a]	$\varphi_n,G_n,g_{n-1},\eta_n,\langle A\rangle_{n-1}$	$D_{\mu0}\eta_n=0$	$\bar{a}_{\mu n},\varphi_n,\bar{G}_{n+1},\bar{g}_n,\bar{\eta}_{n+1},\langle\bar{A}\rangle_n$

[a] The n-fold application of the remainder theorem after completion of the $(n+1)$th cycle yields the additional energy orders, $\bar{\eta}_{n+2}$, $\bar{\eta}_{n+3}$, $\cdots$, $\bar{\eta}_{2n+1}$.

would yield the additional higher orders of the energy $\bar{\eta}_{n+2}$ through $\bar{\eta}_{2n+1}$.

III. THE PV CLASSIFICATION OF PERTURBED VARIATIONAL WAVE FUNCTIONS

A. Introduction

The PV expansions provide a natural, general scheme for the *a priori* classification of all perturbed variational wave functions into three broad categories. These three categories differ in their asymptotic behavior as the perturbing parameter approaches zero. The basis for the classification depends upon the theoretically predictable agreement or lack of agreement of corresponding leading terms in the PV and exact expansions, Eqs. (9) and (11), respectively. The conclusions reached in this manner are valid whether the variational wave functions concerned are optimized by conventional numerical means or order by order via the PV procedure; the results, however, are particularly easy to interpret in terms of PV theory. The three categories of perturbed variational wave functions are derived and contrasted below.[22] Several theoretical applications illustrating the insight obtained from the classification scheme are also presented.

B. Category I Wave Functions

The point of departure in all PV calculations is the optimization of the zero-order energy η_0, which from Eq. (16a) may be written as

$$\eta_0=G_0=\langle\varphi_0|H_0|\varphi_0\rangle\geq\epsilon_0. \tag{29}$$

Thus, Eq. (29) may be considered to represent the application of the variational principle to an approximate solution of the unperturbed Schrödinger equation, Eq. (10). Here φ_0 is formally obtained from the chosen φ by replacing the a_μ with the $a_{\mu0}$, i.e.,

$$\varphi_0=\varphi\{a_{\mu0}\}. \tag{30}$$

If the form of φ is such that φ_0 becomes equal to ψ_0 for special values of the $a_{\mu0}$, then in accordance with the variational principle, the optimization of the η_0, Eq. (29), in respect to all the $a_{\mu0}$, will generate just those special values as the optimum $\bar{a}_{\mu0}$. For such a φ, it follows that

$$\bar{\varphi}_0=\varphi\{\bar{a}_{\mu0}\}=\psi_0, \tag{31a}$$

and from Eqs. (29) and (27a), and RS perturbation theory,[15]

$$\bar{\eta}_0=\langle\psi_0|H_0|\psi_0\rangle=\epsilon_0, \tag{31b}$$

$$\bar{\eta}_1=\langle\psi_0|H_1|\psi_0\rangle=\epsilon_1, \tag{31c}$$

while from the variational principle,

$$\bar{\eta}_2\geq\epsilon_2, \tag{31d}$$

since

$$\sum_{m=2}^{\infty}\bar{\eta}_m\lambda^m\geq\sum_{m=2}^{\infty}\epsilon_m\lambda^m, \tag{31e}$$

where in general, for the higher orders,

$$\bar{\eta}_m\neq\epsilon_m,\quad m\geq3. \tag{31f}$$

All wave functions satisfying Eqs. (31) are designated as category I functions. Such wave functions yield variationally optimized energies correct at least through first order and other expectation values correct at least in zero order. If ψ_0 is known from theory, it is always possible to construct an unlimited number of approximate wave functions belonging to category I by taking ψ_0 as the starting point. Thus, the prototype of this category is obtained by taking φ as ψ_0 with all parameters embedded in ψ_0 fixed at their theoretical values; in this case, there are no adjustable parameters, so

$$\varphi=\bar{\varphi}=\bar{\varphi}_0=\psi_0,\quad \bar{\varphi}_r=0 \text{ for } r\geq1, \tag{32a}$$

and

$$\bar{\eta}=\epsilon_0+\epsilon_1\lambda,\quad \bar{\eta}_m=0 \text{ for } m\geq2. \tag{32b}$$

The accuracy of Eqs. (32) can be systematically improved in the higher orders by again taking φ as ψ_0 but by systematically replacing the theoretically fixed parameters in ψ_0 with variationally determined parameters a_μ; still more elaborate functions may be constructed from ψ_0 by inserting additional parameters and adding other functions containing adjustable parameters. Nevertheless, the conditions of Eqs. (31) will be satisfied if ψ_0 is contained at least implicitly in φ as the optimization of η_0, Eq. (29), will project out ψ_0. In general, the introduction of one or more variational parameters in ψ_0 converts the optimum $\bar{\varphi}$ and $\bar{\eta}$ of Eq. (32) into infinite PV expansions where the leading terms satisfy Eqs. (31). Any improvement in the variational quality of functions of this category is automatically concentrated in improving the quality of second- and higher-order energy terms. The only distinction among category I wave functions, then, is how

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[22] The theory of the PV classification scheme has previously been presented in bare outline in Ref. 3.

accurately the $\bar{\varphi}_r$ for $r \geq 1$ and the $\bar{\eta}_m$ for $m \geq 2$ approximate the corresponding exact terms, ψ_r and ϵ_m. This common feature permits meaningful comparisons to be made among these functions. For example, if follows from Eq. (31d) that all category I wave functions can be arranged on a relative scale of increasing variational accuracy with the criterion being how well $\bar{\eta}_2$ approximates ϵ_2 from above, and hence, from Eq. (27b), how well $\bar{\varphi}_1$ approximates ψ_1.

Under suitable conditions, the agreement between corresponding terms of the optimum $\bar{\varphi}$ and $\bar{\eta}$ expansions and the exact ψ and ϵ expansions can be extended to still higher orders than in Eqs. (31). The second step in the PV procedure consists of finding the stationary value of the first-order energy η_1, which from Eq. (16b) may be written as

$$\eta_1 = G_1 + g_0 = 2\langle\varphi_0|H_0|\varphi_1\rangle + \langle\varphi_0|H_1|\varphi_0\rangle; \qquad (33)$$

here

$$\varphi_1 = W_{1,1}\varphi_0 = \sum_{\mu=1}^{P} (\partial\varphi_0/\partial a_{\mu 0}) a_{\mu 1}, \qquad (34)$$

and the stationary value of η_1 is found by variation of the $a_{\mu 0}$ which in turn yields the optimum $\bar{a}_{\mu 1}$. A general argument in justification of this procedure has been given in the discussion following Eq. (22). Another more specialized argument is the following: The condition that η_1, Eq. (33), have a stationary value in respect to an arbitrary variation of φ_0, subject only to the constraints that φ_0 remain normalized and orthogonal to φ_1 [see Eqs. (18)], leads to the following defining differential equation for φ_0 and φ_1:

$$(H_0 + \alpha)\varphi_1 + (H_1 + \beta)\varphi_0 = 0,$$

where α and β are Lagrangian multipliers; this is seen to be equivalent in form to

$$(H_0 - \epsilon_0)\psi_1 + (H_1 - \epsilon_1)\psi_0 = 0, \qquad (35)$$

i.e., the first-order coupled differential equation of RS perturbation theory.[15] Thus, Eq. (33) is the variational equivalent of Eq. (35). For category I wave functions, it follows that if the form of φ is such that φ_1 becomes equal to ψ_1 for certain values of the $a_{\mu 1}$, then the optimum $\bar{a}_{\mu 1}$ determined via Eq. (33) will correspond to just those values. For such φ,

$$\bar{\varphi}_1 = \bar{W}_{1,1}\varphi_0 = \psi_1, \qquad (36a)$$

$$\bar{\eta}_2 = \langle\psi_0|H_1|\psi_1\rangle = \epsilon_2, \qquad (36b)$$

$$\bar{\eta}_3 = \langle\psi_1|H_1 - \epsilon_1|\psi_1\rangle = \epsilon_3, \qquad (36c)$$

and from the variational principle,

$$\bar{\eta}_4 \geq \epsilon_4, \qquad (36d)$$

since

$$\sum_{m=4}^{\infty} \bar{\eta}_m \lambda^m \geq \sum_{m=4}^{\infty} \epsilon_m \lambda^m, \qquad (36e)$$

where in general, for the higher orders,

$$\bar{\eta}_m \neq \epsilon_m, \quad m \geq 5. \qquad (36f)$$

Here, Eqs. (36b) and (36c) follow from Eqs. (27b), (27c), (35), and (C6), and from RS perturbation theory.[15] Category I wave functions satisfying Eqs. (36), in addition to Eqs. (31), yield variationally optimized energies correct at least through third order and other expectation values correct at least through first order. In analogy with the previous discussion concerning the construction of category I wave functions, if both ψ_0 and ψ_1 are known from theory, approximate wave functions satisfying Eqs. (31) and (36) can always be constructed by taking φ as linear combinations of generalized forms of ψ_0 and ψ_1. This process can be extended to still higher orders if higher orders of the ψ_r are known. In general, it follows from RS perturbation theory[3,15] that if the expansions of $\bar{\varphi}$ and ψ should agree through the nth order, the expansions of $\bar{\eta}$ and ϵ would then agree through the $(2n+1)$th order.

C. Category II Wave Functions

If the form of the chosen φ is such that for no values of the variational parameters $a_{\mu 0}$ can φ_0 become equal to ψ_0, then the optimization of η_0, Eq. (29), will merely produce the variational approximation function $\bar{\varphi}_0$. Thus,

$$\bar{\varphi}_0 = \varphi\{\bar{a}_{\mu 0}\} \neq \psi_0, \qquad (37a)$$

$$\bar{\eta}_0 = \langle\bar{\varphi}_0|H_0|\bar{\varphi}_0\rangle \geq \epsilon_0, \qquad (37b)$$

$$\bar{\eta}_1 = \langle\bar{\varphi}_0|H_1|\bar{\varphi}_0\rangle \neq \epsilon_1, \qquad (37c)$$

and in general, for the higher orders,

$$\bar{\eta}_m \neq \epsilon_m, \quad m \geq 2. \qquad (37d)$$

All wave functions satisfying Eqs. (37) are designated as category II functions. In general, such wave functions yield variationally optimized energies and other expectation values *incorrect* in all orders. Although there is no theoretical basis at present, it has been found in all PV expansions[3,12,23] for atomic isoelectronic sequences with *scaled* category II wave functions that Eq. (37c) may be replaced by the bounded relationship[24]

$$0 \leq \bar{\eta}_1 \leq \epsilon_1. \qquad (37c')$$

Any improvement in the variational quality of functions of this category by the introduction of additional parameters is expended in the improvement of the quality of the *zero-* as well as higher-order terms. It follows from Eq. (37b) that all category II wave functions can be arranged on a relative scale of increasing variational accuracy with the criterion being how well $\bar{\eta}_0$ approximates ϵ_0 from above, and hence, how well $\bar{\varphi}_0$ approximates ψ_0. The introduction of additional parameters in φ cannot eliminate the inherent zero-order error

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[23] J. N. Silverman (unpublished).

[24] The lower bound in Eq. (37c′) applies for all systems, such as atomic isoelectronic sequences, where H_1 is positive definite.

unless in this process sufficient terms are added to introduce ψ_0 implicitly, thus converting φ to a category I wave function.

D. Category III Wave Functions

A third category of perturbed variational wave functions, intermediate in a sense to categories I and II, arises when there is zero-order degeneracy. According to degenerate RS perturbation theory,[15] the correct ψ_0 may be obtained in such cases by diagonalizing the matrix of the degenerate zero-order functions of the proper symmetry, the $\psi_0^{(i)}$, over the perturbation operator. This is entirely equivalent[25] to variationally optimizing the linear mixing coefficients, the b_{i0}, of a linear combination of all these $\psi_0^{(i)}$ in respect to the total Hamiltonian H, yielding the optimum results

$$\psi_0=\sum_i \bar{b}_{i0}\psi_0^{(i)}, \tag{38a}$$

and

$$\bar{\eta}=\langle\psi_0|H|\psi_0\rangle=\epsilon_0+\epsilon_1\lambda. \tag{38b}$$

It should be apparent from the previous discussion that if φ is constructed so as to contain in generalized form only *one* of the $\psi_0^{(i)}$, say $\psi_0^{(k)}$, then the optimization of η_0, Eq. (29), will project out just this $\psi_0^{(k)}$. For such φ,

$$\bar{\varphi}_0=\varphi\{\bar{a}_{\mu 0}\}=\psi_0^{(k)}\neq\psi_0, \tag{39a}$$

$$\bar{\eta}_0=\langle\psi_0^{(k)}|H_0|\psi_0^{(k)}\rangle=\epsilon_0, \tag{39b}$$

but from the variational principle,

$$\bar{\eta}_1^{(k)}=\langle\psi_0^{(k)}|H_1|\psi_0^{(k)}\rangle\geq\epsilon_1, \tag{39c}$$

since

$$\sum_{m=1}^{\infty}\bar{\eta}_m^{(k)}\lambda^m\geq\sum_{m=1}^{\infty}\epsilon_m\lambda^m, \tag{39d}$$

where in general, for the higher orders,

$$\bar{\eta}_m^{(k)}\neq\epsilon_m,\quad m\geq 2. \tag{39e}$$

All wave functions satisfying Eqs. (39) are designated as category III functions. In general, such wave functions yield variationally optimized energies correct *only* in zero order and other expectation values *incorrect* in all orders. It also follows from the variational principle that the $\bar{\eta}_1^{(i)}$ corresponding to the various $\psi_0^{(i)}$ can be arranged in a sequence of relative accuracy,

$$\epsilon_1\leq\bar{\eta}_1^{(1)}\leq\bar{\eta}_1^{(2)}\leq\cdots\leq\bar{\eta}_1^{(i)}\leq\cdots, \tag{40}$$

where for atomic isoelectronic sequences,[26] $\psi_0^{(1)}$ and $\bar{\eta}_1^{(1)}$ correspond to the "lowest" spectroscopic configuration. It follows from Eq. (40) that different category III wave functions, each corresponding to a different $\psi_0^{(i)}$, can be arranged on a coarse relative scale of increasing variational accuracy with the criterion being how well $\bar{\eta}_1^{(i)}$ approximates ϵ_1 from above, and hence, how well $\psi_0^{(i)}$ approximates ψ_0.

A somewhat more refined system of evaluating the relative accuracy of category III wave functions can be developed as follows: Consider a number of category III wave functions all based on different generalized forms of the *same* $\psi_0^{(i)}$, most advantageously taken as $\psi_0^{(1)}$. Any improvement in the quality of such category III wave functions, obtained by inserting additional parameters, cannot in general affect the value of $\bar{\eta}_1^{(1)}$, Eq. (39c), but is restricted to improving the quality of second- and higher-order energy terms. Thus, these functions have a pseudo–category-I character and can be arranged on a relative scale of increasing variational accuracy by comparing their respective values of $\bar{\eta}_2^{(1)}$, which can be considered to bound a hypothetical degenerate $\epsilon_2^{(1)}$ from above. If, however, the process of improving the quality of such a category III φ via the introduction of additional functions containing adjustable parameters should also introduce a generalized form of *another* degenerate $\psi_0^{(i)}$, the corresponding first-order energy levels of Eqs. (40) would be displaced in the characteristic manner by the interaction between the two degenerate zero-order functions, and an improved upper bound to ϵ_1 would be obtained. The introduction of *all* the degenerate $\psi_0^{(i)}$ in generalized form in this manner would culminate in the construction of the ψ_0 of Eq. (38a) in generalized form and in the conversion of the φ in question to a category I wave function; the category I φ based on such generalized ψ_0 have been termed[3] *minimum-configuration* wave functions.

E. Several Theoretical Applications

A significant application of the PV classification scheme lies in resolving a theoretical ambiguity in connection with the accuracy of arbitrary approximate wave functions. It is often asserted that the energy of any state can be calculated correct through first order with *any* optimized variational wave function. From the above discussion, however, it follows that this statement is incorrect when literally applied to optimized energy expansions in powers of a well-defined perturbing parameter; *only* category I wave functions have this desirable characteristic. It also follows that for small enough perturbations, i.e., for small enough values of λ, *all* category I wave functions must be energetically superior to *all* category III wave functions which must in turn be superior to *all* category II wave functions; with increasing λ, of course, this relative sequence of superiority of representative wave functions of the three categories may change due to partial compensation of error among the various energy orders. Silverman and Brigman[3] have made extensive use of the PV classification scheme to categorize a wide variety of variational wave functions for atomic isoelectronic sequences and

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[25] See, for example, L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), pp. 165–172 and 186–189.

[26] See, for example, D. Layzer [Ann. Phys. (N. Y.) **8**, 271 (1959)] and J. Linderberg and H. Shull [J. Mol. Spectry. **5**, 1 (1960)] for calculations of ϵ_1, and $\eta_1^{(i)}$ for various degenerate states of several atomic isoelectronic sequences.

to interpret in this manner apparently anomalous energy trends with varying Z.

The PV expansions have proved to be well suited for the derivation of a number of important theorems applicable to optimized variational quantities. These or similar theorems also apply to the exact quantities and can be derived in an analogous manner via the RS perturbation expansions[27]; this close correspondence between exact and variational quantities is not surprising in view of the formal analogy between the RS and the PV expansions. The remainder theorem, derived in Appendix B, and the variational Hellmann-Feynman theorem, derived in Appendix C, have already been discussed in Sec. IIC in connection with their application in the PV procedure. In addition, the variational integral Hellmann-Feynman theorem is derived in Appendix D, the virial theorem, in abbreviated form, in Appendix E, and a theorem relating to the expectation value $\langle \bar{V}_0 \rangle$, where V_0 is the unperturbed potential operator, in Appendix F. Appendix D also contains an important theoretical application of the variational integral Hellmann-Feynman theorem in conjunction with the PV classification scheme. A general analysis of the scaling parameter and the virial theorem in terms of PV theory is presented in a subsequent paper[13] in this series.

The theorem involving $\langle \bar{V}_0 \rangle$ is of particular interest because it permits an estimate to be made of the asymptotic accuracy of an energetically optimized expectation value other than the energy; this is done by obtaining a relationship between the PV expansions of the property and of the energy. Thus, it follows from Eq. (F4), Appendix F, that the PV expansion of the optimum $\langle \bar{r}^{-1} \rangle$ for an atomic isoelectronic sequence is given in Hartree atomic units[1,28] by

$$\langle \bar{r}^{-1} \rangle = Z \langle \bar{R}^{-1} \rangle = \sum_{m=0}^{\infty} (m-2) \bar{\eta}_m Z^{1-m}. \tag{41}$$

It has been empirically determined that the expectation value of r^{-1}, which is proportional to the diamagnetic nuclear shielding,[29] is in some instances extraordinarily insensitive to the quality of the variational wave function used in its computation; for example, this has been observed[30] for the ground state of the He isoelectronic sequence for variational wave functions ranging from the simplest to the most elaborate form. This behavior can be readily interpreted via the PV classification scheme. It is apparent from Eqs. (31), (37), (39), and (41) that $\langle \bar{r}^{-1} \rangle$ is obtained correct through second order with all category I wave functions, and, aside from the vanishing second-order term, incorrect in all orders with all category II wave functions, and correct only in zero order with all category III wave functions. Therefore, with increasing Z, values of $\langle \bar{r}^{-1} \rangle$ computed with different category I wave functions should rapidly converge to the correct values, values computed with different category II wave functions should eventually diverge linearly with Z below the correct values, and values computed with different category III wave functions based on the same generalized degenerate $\psi_0^{(i)}$ should rapidly converge to common values lying below the correct values by a constant amount. These predictions are borne out by the previously cited[30] He sequence calculations, all of which were performed with category I wave functions; insufficient variational data are available[31] at present for an adequate test of the predictions concerning category II and III wave functions. Equation (41) has previously been used by Hall[32] to compute the expectation value of r^{-1} for the He isoelectronic sequence with the RS expansion of the exact ϵ, determined variationally by Hylleraas and Midtdal.[2]

The PV classification may also be applied to the *a priori* analysis of the variational parameters embedded in the variational wave functions. Thus, for category I wave functions, it is possible to subdivide all the a_μ into three principal types of parameters, designated as the b_π, c_ρ, and d_σ, respectively. For these, the optimum $\bar{b}_{\pi 0}$ and $\bar{c}_{\rho 0}$ can be determined merely by inspection and comparison of φ and ψ_0 while the $\bar{d}_{\sigma 0}$ cannot be so determined. The b_π are those parameters which can be brought into correspondence with the theoretically known parameters embedded in ψ_0 so the $\bar{b}_{\pi 0}$ are given by just these theoretical values; the c_ρ represent additional parameters inserted in φ in such a manner so that the $\bar{c}_{\rho 0}$ must vanish identically to satisfy Eq. (31a); the d_σ represent those additional parameters inserted in φ in such a manner so that the $\bar{d}_{\sigma 0}$ are indeterminate from the comparison of φ and ψ_0. Then, Eq. (31a) can be replaced by the more general condition for category I wave functions,

$$\begin{aligned} \bar{\varphi}_0 &= \varphi\{\bar{b}_{\pi 0};\, \bar{c}_{\rho 0};\, \bar{d}_{\sigma 0}\} \\ &= \varphi\{\bar{b}_{\pi 0};\, 0;\, d_{\sigma 0}\} = \psi_0. \end{aligned} \tag{31a$'$}$$

In the discussion following Eq. (25a), it was noted that, in general, the zero-order parameters appear nonlinearly in the zero-order set of PV variational equations while the successive higher orders of the parameters appear linearly in the successive higher-order variational equations; thus, a marked reduction

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[27] See P.-O. Löwdin, [J. Mol. Spectry. 3, 46 (1959)] for a comprehensive review of the virial, Hellmann-Feynman, and other related theorems, with applications to perturbation theory.

[28] We reserve the symbols r and r_i for radial coordinates in Hartree atomic units and R and R_i for the corresponding quantities in modified atomic units; to convert results expressed in modified atomic units to Hartree atomic units, multiply energies by Z^2 and expectation values of the type $\langle \bar{R}^n \rangle$ by Z^{-n}; see also Ref. 1.

[29] W. E. Lamb, Jr., Phys. Rev. **60**, 817 (1941).

[30] J. N. Silverman, O. Platas, and F. A. Matsen, J. Chem. Phys. **32**, 1402 (1960), Tables IV and XI.

[31] F. T. Ormond and F. A. Matsen, J. Chem. Phys. **30**, 368 (1959), Table I; the Li and Be sequence closed- and open-shell calculations reported here were performed with category II wave functions but were not computed for sufficiently large values of Z to reveal the asymptotic behavior.

[32] G. G. Hall, Phil. Mag. **6**, 249 (1961).

in the PV computational labor can be achieved by the *a priori* evaluation of some or all of the $\bar{a}_{\mu 0}$.

An important example of the type-b_π parameter is a scaling parameter k inserted to insure that $\bar{\varphi}$ satisfies the virial theorem[27]; it is easy to show[13,33] that $\bar{k}_0=1$ for all category I wave functions.

Examples of the type-c_ρ parameter are furnished by the linear coupling coefficients for functions added to a generalized ψ_0 in the construction of a category I wave function. It should be noted that the $\bar{c}_\rho$ expansions must vanish in zero order but need not vanish in higher orders; thus, the $\bar{c}_\rho$ expansions have the general form

$$\bar{c}_\rho=\sum_{j=1}^{\infty} \bar{c}_{\rho j}\lambda^j, \tag{42}$$

in agreement with the previously empirically determined[4] behavior of the linear mixing coefficients in category I configuration-interaction wave functions for the He isoelectronic sequence.

Another example of the type-c_ρ parameter worthy of special note arises in some category I open-shell[34] wave functions. For the ground state of the He isoelectronic sequence, Scherr and Silverman[4] have found that the optimum orbital exponents, and hence the optimum orbitals, of a simple analytic category I open-shell wave function do not have a normal PV expansion but rather can only be expanded in powers of $\lambda^{1/2}$. For the analytic function considered, the open-shell character can be formulated in terms of an orbital-splitting parameter x. In Appendix G, it is shown via a simple argument based on PV theory that the anomalous expansions result from the fact that the optimum $\bar{x}^2$ must be a type-$\bar{c}_\rho$ parameter described by Eq. (42). Stewart[35] and other authors[36] have subsequently shown that these anomalous orbital expansions persist when the much more general open-shell, or so-called unrestricted, Hartree-Fock orbitals are used to construct this He sequence open-shell wave function; thus, the anomaly is not an artifact of the simple analytic orbitals originally used, but represents a fundamental characteristic of this type of wave function. A general explanation of this anomalous behavior from the standpoint of PV theory is outlined in Appendix G. In essence, this variety of PV orbital expansion arises whenever the quadratic integral $\langle\bar{\varphi}_x|\,\bar{\varphi}_x\rangle$, in analogy with $\bar{x}^2$, must have a $\bar{c}_\rho$-type of expansion, i.e., whenever $\langle\bar{\varphi}_{x0}|\,\bar{\varphi}_{x0}\rangle=0$; here, φ_x is a generalized splitting orbital.

The indeterminate d_σ-type parameters of category I wave functions are usually encountered in configuration-interaction functions formed by taking a linear combination of a generalized ψ_0 with one or more additional functions χ. The optimum linear coefficients of the χ must, of course, vanish in zero order; if, however, the χ contain nonlinear parameters which are *not* present in the generalized ψ_0, the $\bar{\chi}_0$ may contain nonvanishing $\bar{d}_{\sigma 0}$ which must be computed via the PV procedure. An example of such a parameter is furnished by the orbital exponent of the $(2p)^2$ configuration function added to category I wave functions for the He isoelectronic sequence.[4]

For category II wave functions, it is predicted from PV theory that in general all variational parameters are of the same type with the normal PV expansions of Eq. (9a). It is not possible, however, to determine any of the expansion orders of the optimum parameters in an *a priori* manner; thus, the $\bar{a}_{\mu 0}$ must be computed via the PV procedure. Some guidance in the iterative numerical calculation of the $\bar{a}_{\mu 0}$ may be obtained from empirical rules such as those due to Slater[37]; alternatively, if ψ_0 is known, and the category II wave function in question resembles a generalized ψ_0, the $\bar{a}_{\mu 0}$ may lie close[5,12] to the corresponding theoretical values in ψ_0. Since the type-$\bar{c}_\rho$ parameter of Eq. (42) does not generally appear in category II wave functions, the previously described anomalous behavior of optimum orbital exponents and orbitals for some category I open-shell wave functions *cannot occur* for a corresponding category II open-shell wave function. Thus, as shown in Appendix G, for category II wave functions, $\bar{x}_0{}^2\neq 0$, or more generally, $\langle\bar{\varphi}_{x0}|\,\bar{\varphi}_{x0}\rangle\neq 0$. If $\bar{x}_0{}^2>0$, the orbital exponents and the corresponding orbitals would have normal PV expansions in terms of real quantities; if, however, $\bar{x}_0{}^2<0$, the orbital exponent and corresponding orbital PV expansions would be in terms of complex quantities. The former behavior has subsequently been verified[12] for some category II open-shell wave functions for the He isoelectronic sequence; the latter behavior has previously been empirically determined[5] for a category II open-shell wave function for the Li isoelectronic sequence, and has been conjectured[3] for an analogous wave function[38] for the B isoelectronic sequence.

As previously mentioned, category III wave functions based on generalized forms of a given degenerate $\psi_0{}^{(i)}$ have a pseudo-category-I character. Therefore, the above discussion concerning the variational parameters of category I wave functions applies in its entirety to such category III wave functions. The only peculiarity worthy of special note arises when a generalized form of another degenerate $\psi_0{}^{(i)}$ is added to the initial function. In such cases, the optimum linear coupling coefficient of the added function no longer vanishes in zero order and must be computed by the PV procedure. If generalized forms of *all* the degenerate $\psi_0{}^{(i)}$ are added in this manner, the minimum-configuration[3]

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[33] W. Kohn, Phys. Rev. **71**, 635 (1947).

[34] See Ref. 3 for a definition of closed- and open-shell wave functions and for an extensive bibliography of such calculations for atomic systems.

[35] A. L. Stewart, Proc. Phys. Soc. (London) **83**, 1033 (1964).

[36] C. A. Coulson, Proc. Phys. Soc. (London) **84**, 511 (1964); J. L. J. Rosenfeld and D. D. Konawalow, J. Chem. Phys. **41**, 3556 (1964); C. Froese, Phys. Rev. **140**, A1489 (1965).

[37] J. C. Slater, Phys. Rev. **36**, 57 (1930).

[38] G. H. Brigman and J. N. Silverman, J. Chem. Phys. **44**, 3136 (1966).

category I wave function is formed, and the optimum linear coupling coefficients are given in zero order by the $\bar{b}_{i0}$ of Eq. (38a).

These parametric considerations have been applied in a series of PV calculations for the helium[12] and lithium[39] isoelectronic sequences with category I and category II wave functions.

IV. CONCLUSIONS

The PV procedure may be regarded as a generalized extrapolation scheme which yields energetically optimized approximate solutions for a perturbed system in the form of Taylor expansions about either *exact* or *optimized approximate* solutions to a simpler, unperturbed system. The PV procedure is thus of wider applicability than RS perturbation theory because the latter approach, unlike the former, requires that the exact unperturbed solution be known; in the PV procedure, any analytic wave function containing a number of adjustable parameters may serve as the input function for the unperturbed system.

The PV expansions obtained as output serve a dual purpose: (1) They furnish specific variational data as a function of the perturbation for the systems and wave functions considered; and (2) they provide a general framework for the systematic classification and evaluation of all perturbed variational wave functions in respect to their quality. It is this interpretive aspect of the PV expansions which is of particular interest because it affords an insight into the relative behavior of variational wave functions which cannot be obtained via the conventional variational approach.

The PV procedure is applicable to all systems for which the Hamiltonian may be written in the form of Eqs. (2). Atomic isoelectronic sequences have previously been mentioned as an important example of such systems. There are numerous other possible applications such as atomic systems perturbed by electric and magnetic fields, and nonrelativistic formulations of such systems perturbed by relativistic effects. Any previously derived analytic variational solution for the unperturbed system may serve as the starting point in these calculations; if such a function is used, the optimum zero-order parameters are already known. The effect of the perturbation on the variational parameters, the wave function, and associated expectation values, may then be followed to any desired order via the PV procedure.

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APPENDIX A: THE VARIATIONAL WAVE OPERATOR

Consider the functional

$$X=X(a_1,a_2,\cdots,a_P)\equiv X\{a_\mu\}\,, \qquad \text{(A1)}$$

where the a_μ are undetermined analytic functions of the independent variable λ, which can be expanded in Taylor series about $\lambda=0$:

$$a_\mu=a_\mu(\lambda)=\sum_{j=0}^{\infty} a_{\mu j}\lambda^j;\quad \mu=1,2,\cdots,P, \qquad \text{(A2a)}$$

where

$$a_{\mu j}\equiv(j!)^{-1}\left(\frac{d^j a_\mu}{d\lambda^j}\right)_{\lambda=0}. \qquad \text{(A2b)}$$

We seek the explicit form of the X_m in the analogous expansion of X about $\lambda=0$,

$$X=\sum_{m=0}^{\infty} X_m\lambda^m, \qquad \text{(A3a)}$$

where

$$X_m\equiv(m!)^{-1}\left(\frac{d^m X}{d\lambda^m}\right)_{\lambda=0}. \qquad \text{(A3b)}$$

Since the $a_\mu\rightarrow a_{\mu 0}$ as $\lambda\rightarrow 0$, equivalent results are obtained by expanding X about the $a_{\mu 0}$; in the usual notation, the Taylor expansion of a function of P variables can be written as

$$X\{a_\mu\}=\sum_{k=0}^{\infty}(k!)^{-1}\times\left[\sum_{\mu=1}^{P}(a_\mu-a_{\mu 0})\left(\frac{\partial}{\partial a_\mu}\right)_{a_\mu=a_{\mu 0}}\right]^k X\{a_\mu\}. \qquad \text{(A4)}$$

The as yet undetermined $a_{\mu 0}$ may be treated as dummy variables so it follows that

$$\left[\frac{\partial}{\partial a_\mu}X\{a_\mu\}\right]_{a_\mu=a_{\mu 0}}\equiv\frac{\partial}{\partial a_{\mu 0}}X\{a_{\mu 0}\}. \qquad \text{(A5)}$$

Then, Eq. (A4) can be written in the form

$$X\{a_\mu\}=\sum_{k=0}^{\infty}(k!)^{-1}\left[\sum_{\mu=1}^{P}\sum_{j=1}^{\infty}a_{uj}\lambda^j D_{\mu 0}\right]^k X\{a_{\mu 0}\}\,, \qquad \text{(A6)}$$

where we have substituted Eq. (A2a) and introduced the notation

$$D_{\mu 0}\equiv\frac{\partial}{\partial a_{\mu 0}}. \qquad \text{(A7)}$$

Upon changing the order of summation and introducing the additional notation

$$d_j\equiv\sum_{\mu=1}^{P}a_{\mu j}D_{\mu 0}\,, \qquad \text{(A8)}$$

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[39] J. N. Silverman and D. N. Peden (to be published).

TABLE II. Constraints[a] of $W_{m,m}$ operator for $1\leq m\leq 7$.

m	k	j	k_j
1	1	1	$k_1=1$
2	1	2	$k_2=1$
	2	1	$k_1=2$
3	1	3	$k_3=1$
	2	1,2	$k_1=1$, $k_2=1$
	3	1	$k_1=3$
4	1	4	$k_4=1$
	2	1,3	$k_1=1$, $k_3=1$
	2	2	$k_2=2$
	3	1,2	$k_1=2$, $k_2=1$
	4	1	$k_1=4$
5	1	5	$k_5=1$
	2	1,4	$k_1=1$, $k_4=1$
	2	2,3	$k_2=1$, $k_3=1$
	3	1,2	$k_1=1$, $k_2=2$
	3	1,3	$k_1=2$, $k_3=1$
	4	1,2	$k_1=3$, $k_2=1$
	5	1	$k_1=5$
6	1	6	$k_6=1$
	2	1,5	$k_1=1$, $k_5=1$
	2	2,4	$k_2=1$, $k_4=1$
	2	3	$k_3=2$
	3	1,4	$k_1=2$, $k_4=1$
	3	1,2,3	$k_1=1$, $k_2=1$, $k_3=1$
	3	2	$k_2=3$
	4	1,2	$k_1=2$, $k_2=2$
	4	1,3	$k_1=3$, $k_3=1$
	5	1,2	$k_1=4$, $k_2=1$
	6	1	$k_1=6$
7	1	7	$k_7=1$
	2	1,6	$k_1=1$, $k_6=1$
	2	2,5	$k_2=1$, $k_5=1$
	2	3,4	$k_3=1$, $k_4=1$
	3	1,3	$k_1=1$, $k_3=2$
	3	1,5	$k_1=2$, $k_5=1$
	3	1,2,4	$k_1=1$, $k_2=1$, $k_4=1$
	3	2,3	$k_2=2$, $k_3=1$
	4	1,2	$k_1=1$, $k_2=3$
	4	1,4	$k_1=3$, $k_4=1$
	5	1,2	$k_1=3$, $k_2=2$
	5	1,3	$k_1=4$, $k_3=1$
	6	1,2	$k_1=5$, $k_2=1$
	7	1	$k_1=7$

[a] Positive integral solutions of Eqs. (A13b) and (A13c).

we obtain from Eq. (A6)

$$X\{a_\mu\}=\sum_{k=0}^{\infty}(k!)^{-1}[\sum_{j=1}^{\infty}d_j\lambda^j]^k X\{a_{\mu 0}\}. \tag{A9}$$

It follows from the multinomial theorem that

$$[\sum_{j=1}^{\infty}d_j\lambda^j]^k=k!\sum_{k_j}\prod_{j=1}^{\infty}\frac{(d_j\lambda^j)^{k_j}}{k_j!}, \tag{A10}$$

subject to the positive integral solutions of the constraint

$$\sum_{j=1}^{\infty}k_j=k. \tag{A11}$$

Then, subject to Eq. (A11),

$$X\{a_\mu\}=\sum_{k=0}^{\infty}\sum_{k_j}\left[\prod_{j=1}^{\infty}\frac{d_j^{k_j}}{k_j!}X\{a_{\mu 0}\}\right]\lambda^B, \tag{A12a}$$

where

$$B=\sum_{j=1}^{\infty}jk_j. \tag{A12b}$$

Thus, by comparing coefficients of like powers of λ in Eqs. (A3a) and (A12a), we obtain the general result

$$X_m=\sum_{k=1}^{m}\sum_{k_j}\prod_{j=1}^{m}\frac{d_j^{k_j}}{k_j!}X\{a_{\mu 0}\},\quad m\geq 1 \tag{A13a}$$

subject to the positive integral solutions of the constraints,

$$\sum_{j=1}^{m}k_j=k, \tag{A13b}$$

and

$$\sum_{j=1}^{m}jk_j=m; \tag{A13c}$$

the special case of $m=0$ corresponds to $k=0$ and yields

$$X_0=X\{a_{\mu 0}\}. \tag{A13d}$$

The summation limits over k and j in Eqs. (A13) can be derived from a straightforward consideration of the nature of the constraints. The summation over k in Eq. (A13a) is required because for $m\geq 2$, the constraint of Eq. (A13c) is satisfied in general by different distributions of k_j corresponding to different values of k.

It proves useful to introduce the multinomial differential operator $W_{m,n}$ defined as

$$W_{m,n}\equiv\sum_{k=1}^{m}\sum_{k_j}\prod_{j=1}^{n}\frac{d_j^{k_j}}{k_j!},\quad m\geq n\geq 1 \tag{A14a}$$

subject to the positive integral solutions of the constraints,

$$\sum_{j=1}^{n}k_j=k, \tag{A14b}$$

and

$$\sum_{j=1}^{n}jk_j=\mathrm{m}. \tag{A14c}$$

In this notation, the first subindex in $W_{m,n}$ gives the order of the highest derivative, while the second subindex gives the order of the highest expansion term of the a_μ; in addition, the special case of $m=n=0$ is defined as

$$W_{0,0}\equiv 1, \tag{A14d}$$

while for all other combinations of indices such as $m<n$ or for negative indices, the operator is defined as zero. The application of the $W_{m,n}$ operator in the asymmetric case of $m>n\geq 1$ is discussed in Appendix B. In the symmetric case of $m=n\geq 0$, the $W_{m,m}$ operator is directly applicable to Eqs. (A13), yielding

$$X_m=W_{m,m}X_0,\quad m\geq 0. \tag{A15}$$

As an aid in calculations, the various solutions of k, j, and k_j satisfying the constraints of the symmetric $W_{m,m}$ operator, Eqs. (A13b) and (A13c), for $1\leq m\leq 7$ are collected in Table II. It should be noted that for $m\geq 1$, it follows quite generally from the constraints that the only solutions for $j=m$ are $k_m=1$ and $k=1$ and that no other solutions of j and k_j are possible for $k=1$; as a consequence, the highest-order expansion terms of the a_μ, the $a_{\mu m}$, occur only linearly in $W_{m,m}$ and are localized in the leading d_m. In addition, it is easy to see that it is always possible to find k_j and k values which satisfy the constraints for $j=m-1, m-2, \cdots, 1$. Thus, including the zero-order parameters contained in X_0, X_m is in general a function of all $a_{\mu j}$ for $0\leq j\leq m$.

By introduction of the total operator W, defined as

$$W=\sum_{m=0}^{\infty} W_{m,m}\lambda^m, \tag{A16}$$

the Taylor expansion of Eq. (A3a) can be written as

$$X=WX_0. \tag{A17}$$

Löwdin[40] has introduced a so-called wave operator for generating the perturbed eigenfunction ψ from the unperturbed eigenfunction ψ_0. In analogy with his terminology, W is designated as the *variational* wave operator since it generates the perturbed approximate function from the corresponding unperturbed approximate function.

The above considerations are readily extended to the product of two or more functionals. To illustrate the simplest case, which is all we need consider here, let

$$F\{a_\mu\}=X\{a_\mu\}Y\{a_\mu\}, \tag{A18}$$

where X and Y are two different functionals, each containing the same set of a_μ. Since the Taylor series of a product equals the product of the Taylor series, it follows immediately that

$$F=WF_0=W(XY)_0=(WX_0)(WY_0), \tag{A19}$$

and that

$$F_m=W_{m,m}F_0=\sum_{r=0}^{m}(W_{r,r}X_0)(W_{m-r,m-r}Y_0),\ m\geq 0. \tag{A20}$$

Further, it is not difficult to determine the effect of the asymmetric operator $W_{m,n}$ on such a product; of particular importance are the cases $m=2n$, $m=2n+1$, and $m=2n-1$, which yield, respectively,

$$W_{2n,n}F_0=\sum_{r=0}^{n-1}[(W_{r,r}X_0)(W_{2n-r,n}Y_0)+(W_{2n-r,n}X_0)(W_{r,r}Y_0)]+(W_{n,n}X_0)(W_{n,n}Y_0), \tag{A21a}$$

$$W_{2n+1,n}F_0=\sum_{r=0}^{n}[(W_{r,r}X_0)(W_{2n+1-r,n}Y_0)+(W_{2n+1-r,n}X_0)(W_{r,r}Y_0)], \tag{A21b}$$

and

$$W_{2n-1,n}F_0=\sum_{r=0}^{n-1}[(W_{r,r}X_0)(W_{2n-1-r,n}Y_0)+(W_{2n-1-r,n}X_0)(W_{r,r}Y_0)]. \tag{A21c}$$

APPENDIX B: THE REMAINDER THEOREM

It follows from the discussion in Sec. IIB and Appendix A that the even and the odd orders of the energy expansion can be respectively expressed in terms of the variational wave operator as

$$\eta_{2n}=W_{2n,2n}G_0+W_{2n-1,2n-1}g_0, \tag{B1a}$$

and

$$\eta_{2n+1}=W_{2n+1,2n+1}G_0+W_{2n,2n}g_0, \tag{B1b}$$

for $n\geq 0$. Equations (B1), however, have not yet been reduced to their most useful form. The desired simplification can be achieved by suitable rearrangement of the variational wave operator. By way of illustration, consider the $W_{2n,2n}$ operator,

$$W_{2n,2n}\equiv\sum_{k=1}^{2n}\sum_{k_j}\prod_{j=1}^{2n}\frac{d_j^{k_j}}{k_j!}, \tag{B2}$$

subject to the constraints,

$$\sum_{j=1}^{2n}k_j=k, \tag{B3a}$$

and

$$\sum_{j=1}^{2n}jk_j=2n. \tag{B3b}$$

From the constraints, it is apparent that for $j=s$, where $n+1\leq s\leq 2n$, the only possible solutions of Eqs. (B3) for k_s are $k_s=1$, i.e., the corresponding d_s must occur linearly in $W_{2n,2n}$; further, these d_s can only occur in products with other d_j for which $j\leq n-1$. Thus, the factoring of d_s from a typical term of this type in Eq. (B2) for a given k and a given distribution of the k_j yields

$$\sum_{j=1}\frac{d_j^{k_j}}{k_j!}=d_s\sum_{j=1}^{2n-s}\frac{d_j^{k_j}}{k_j!},\quad n+1\leq s\leq 2n \tag{B4}$$

where the d_j and k_j on the right-hand side of Eq. (B4) are subject to the modified constraints

$$\sum_{j=1}^{2n-s}k_j=k-1, \tag{B5a}$$

and

$$\sum_{j=1}^{2n-s}jk_j=2n-s; \tag{B5b}$$

for the special case of $s=2n$, the right-hand side of Eq. (B4) reduces to the single term d_{2n}. The systematic factoring of all d_s in Eq. (B2) yields

$$W_{2n,2n}=d_{2n}+\sum_{s=n+1}^{2n-1}d_s\sum_{k=1}^{2n-s}\sum_{k_j}\prod_{j=1}^{2n-s}\frac{d_j^{k_j}}{k_j!}+\sum_{k=1}^{2n}\sum_{k_j}\prod_{j=1}^{n}\frac{d_j^{k_j}}{k_j!}, \tag{B6}$$

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[40] P.-O. Löwdin, J. Math. Phys. 3, 969 (1962); Rev. Mod. Phys. 35, 702 (1963).

where all the remaining terms, which do not contain the d_s, are collected in the last expression on the right-hand side. Then, it follows from Eqs. (A13), (A14), and (B5) that Eq. (B6) can be written as

$$W_{2n,2n}=\sum_{s=n+1}^{2n} d_s W_{2n-s,2n-s}+W_{2n,n}, \qquad \text{(B7a)}$$

which is the desired final form. In an analogous manner, it is easily shown that the $W_{2n+1,2n+1}$ and $W_{2n-1,2n-1}$ operators can be respectively expressed as

$$W_{2n+1,2n+1}=\sum_{s=n+1}^{2n+1} d_s W_{2n+1-s,2n+1-s}+W_{2n+1,n}, \qquad \text{(B7b)}$$

and

$$W_{2n-1,2n-1}=\sum_{s=n+1}^{2n-1} d_s W_{2n-1-s,2n-1-s}+W_{2n-1,n}. \qquad \text{(B7c)}$$

The appropriate substitution of Eqs. (B7) in Eq. (B1a) yields

$$\eta_{2n}=\sum_{s=n+1}^{2n} d_s(W_{2n-s,2n-s}G_0+W_{2n-1-s,2n-1-s}g_0)+W_{2n,n}G_0+W_{2n-1,n}g_0, \qquad \text{(B8)}$$

which reduces to

$$\eta_{2n}=\sum_{s=n+1}^{2n} d_s\eta_{2n-s}+W_{2n,n}G_0+W_{2n-1,n}g_0, \qquad \text{(B9a)}$$

via the expression for the general expansion term of η, Eq. (21); in an analogous manner, Eq. (B1b) can be transformed to

$$\eta_{2n+1}=\sum_{s=n+1}^{2n+1} d_s\eta_{2n+1-s}+W_{2n+1,n}G_0+W_{2n,n}g_0. \qquad \text{(B9b)}$$

Let us now suppose that the first $(n+1)$ sets of variational equations obtained from Eqs. (24) have been solved, thus yielding the optimum $\bar{a}_\mu$ expansions through the nth order. It follows from the definition of d_j, Eq. (A8), that the substitution of these optimum parameters in Eqs. (B9) causes the summations over s to vanish identically. Thus, the optimum energy expansion terms can be expressed solely in terms of the remainder functions, i.e.,

$$\bar\eta_{2n}=\bar W_{2n,n}G_0+\bar W_{2n-1,n}g_0, \qquad \text{(B10a)}$$

and

$$\bar\eta_{2n+1}=\bar W_{2n+1,n}G_0+\bar W_{2n,n}g_0 \qquad \text{(B10b)}$$

for $n\geq 0$; this result is termed the *remainder theorem.* It also follows in an analogous manner from Eqs. (B7) and (25a) that

$$\bar G_m=(\bar d_m+\bar W_{m,m-1})G_0=\bar W_{m,m-1}G_0, \quad m\geq 1; \qquad \text{(B11)}$$

Eq. (B11) may be regarded as a much weaker application of the remainder theorem. It should be noted that Eqs. (B1) and (B9) are valid for both unoptimized and optimized energies, while Eqs. (B10) and (B11) only apply to optimized $\bar\eta$ and $\bar G$, respectively.

APPENDIX C: THE VARIATIONAL HELLMANN-FEYNMAN THEOREM

For a variational wave function of the form of Eq. (3), where all the a_μ are arbitrary differentiable functions of the independent variable λ, it follows from Eq. (5) that

$$\frac{d\eta}{d\lambda}=\sum_{\mu=1}^{P}\frac{\partial\eta}{\partial a_\mu}\frac{da_\mu}{d\lambda}+\frac{\partial\eta}{\partial\lambda}; \qquad \text{(C1)}$$

here,

$$\frac{\partial\eta}{\partial a_\mu}=\left\langle\frac{\partial\varphi}{\partial a_\mu}|H(\lambda)|\varphi\right\rangle+\left\langle\varphi|H(\lambda)|\frac{\partial\varphi}{\partial a_\mu}\right\rangle; \qquad \text{(C2a)}$$

$$\mu=1,2,\cdots,P,$$

and

$$\frac{\partial\eta}{\partial\lambda}=\left\langle\varphi\left|\frac{dH}{d\lambda}\right|\varphi\right\rangle=\left\langle\frac{dH}{d\lambda}\right\rangle. \qquad \text{(C2b)}$$

The total-derivative notation in Eq. (C1) indicates that λ is considered to be the only independent variable; there is no difficulty in generalizing these results to the case where H depends on several independent variables.[41] If the optimum $\bar{a}_\mu$ have been variationally determined, it follows from Eqs. (7) that the substitution of these optimum parameters in Eq. (C1) causes the summation over μ to vanish. Then, for optimum $\bar\varphi$ and $\bar\eta$, and for the specialized H of Eq. (2a),

$$d\bar\eta/d\lambda=\partial\bar\eta/\partial\lambda=\langle\bar\varphi|H_1|\bar\varphi\rangle=\langle\bar H_1\rangle=\bar g, \qquad \text{(C3a)}$$

and for the general H of Eq. (2b),[14] analogously,

$$\frac{d\bar\eta}{d\lambda}=\frac{\partial\bar\eta}{\partial\lambda}=\left\langle\bar\varphi\left|\frac{dH}{d\lambda}\right|\bar\varphi\right\rangle=\sum_{t=1}^{\infty} t\langle\bar H_t\rangle\lambda^{t-1}. \qquad \text{(C3b)}$$

Equation (C3a) or (C3b) is also applicable to the exact ψ and ϵ and, as such, is termed the Hellmann-Feynman theorem[42]; the usual proof for exact quantities, however, depends upon ψ and ϵ satisfying Eq. (1) rather than upon the specific optimization of adjustable parameters. We term either of Eqs. (C3) the *variational* Hellmann-Feynman theorem to emphasize that variationally optimized functions are involved. The above proof was first put forth by Hurley[43]; subsequently there has been considerable discussion[44] as to the general applicability of the variational Hellmann-Feynman theorem. For our purposes, it is sufficient to specify that the φ of Eq. (3) is to be constructed so as to satisfy

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[41] See, for example, E. M. Roberts, Phys. Rev. **128**, 1381 (1962).

[42] H. Hellmann, *Einführung in die Quantenchemie* (Deuticke, Vienna, 1937); R. P. Feynman, Phys. Rev. **56**, 340 (1939); see also J. I. Musher [Am. J. Phys. **34**, 267 (1966)] for a historical disucssion of this theorem.

[43] A. C. Hurley, Proc. Roy. Soc. (London) **A226**, 179 (1954).

[44] See, for example, C. A. Coulson and A. C. Hurley, J. Chem. Phys. **37**, 448 (1962); A. C. Hurley, *ibid.* **37**, 449 (1962), and references cited therein.

the requirements of Hurley's[43] floating functions or of Hall's[32] stable functions; this ensures that Eqs. (C3) are satisfied.

From Eqs. (9c), (15), (19e), and (C3a), we obtain for the PV expansion of the optimum $\bar{\eta}$,

$$\bar{\eta}_m = m^{-1}\bar{g}_{m-1}, \quad m \geq 1. \tag{C4}$$

In addition, by combining Eqs. (21) and (C4), we obtain the alternate relations for the PV expansions,

$$\bar{G}_m + m^{-1}(m-1)\bar{g}_{m-1} = 0, \quad m \geq 1 \tag{C5}$$

and

$$(m-1)\bar{\eta}_m = -\bar{G}_m, \quad m \geq 0. \tag{C6}$$

In the variational wave-operator representation, Eq. (C6) can be reduced by one parametric order via Eq. (B11) of Appendix B; this yields

$$(m-1)\bar{\eta}_m = -\bar{W}_{m,m}G_0 = -\bar{W}_{m,m-1}G_0, \quad m \geq 1. \tag{C7}$$

Since the exact ψ and ϵ satisfy the Hellmann-Feynman theorem, the RS perturbation expansions must also satisfy Eqs. (C4)–(C6); these or equivalent relations for the exact quantities have previously been derived independently by Carr,[20] Fröman,[45] and Scherr and Knight,[16] and have been discussed by Löwdin.[27]

APPENDIX D: THE VARIATIONAL INTEGRAL HELLMANN-FEYNMAN THEOREM

Consider the identity

$$\langle \varphi | H - \eta | \varphi \rangle \equiv 0. \tag{D1}$$

For H given by Eq. (2a), we obtain by suitable rearrangement of Eq. (D1)

$$\langle \varphi_0 | H_0 - \eta_0 | \varphi \rangle + \langle \varphi_0 | H_1\lambda - (\eta - \eta_0) | \varphi \rangle + \langle \varphi - \varphi_0 | H - \eta | \varphi \rangle = 0, \tag{D2}$$

which can be written in the form

$$\left[(\eta - \eta_0) - \frac{\langle \varphi_0 | H_1 | \varphi \rangle \lambda}{\langle \varphi_0 | \varphi \rangle} \right] \langle \varphi_0 | \varphi \rangle = \Delta, \tag{D3a}$$

where

$$\Delta \equiv \langle \varphi_0 | H_0 - \eta_0 | \varphi \rangle + \langle \varphi - \varphi_0 | H - \eta | \varphi \rangle. \tag{D3b}$$

Equations (D1)–(D3) are valid for arbitrary, unoptimized, normalized φ. In general, for such φ, there is no requirement for Δ to vanish. Consider, however, the special case where $\varphi = \psi$ and, hence, $\eta = \epsilon$, $\varphi_0 = \psi_0$, and $\eta_0 = \epsilon_0$. Then it follows from Eqs. (1) and (10) that Δ vanishes, and from Eq. (D3a), we obtain for the exact energy shift in passing from the unperturbed to the perturbed state

$$\epsilon - \epsilon_0 = \langle \psi | H | \psi \rangle - \langle \psi_0 | H_0 | \psi_0 \rangle = \langle \psi_0 | H_1 | \psi \rangle \lambda / \langle \psi_0 | \psi \rangle. \tag{D4}$$

Equation (D4), which was originally derived in another manner by Breit,[46] and independently by Parr[47] and Richardson and Pack,[48] has been termed the integral Hellmann-Feynman theorem by Parr.[47]

The question naturally arises whether Δ vanishes when computed with energetically optimized approximate functions. By substituting the PV expansions of the optimum $\bar{\varphi}$ and $\bar{\eta}$, Eqs. (9b) and (9c), in Eq. (D3b), we obtain the following PV expansion for the optimum $\bar{\Delta}$:

$$\bar{\Delta} = \sum_{m=0}^{\infty} \bar{\Delta}_m \lambda^m, \tag{D5}$$

where

$$\bar{\Delta}_0 = \langle \bar{\varphi}_0 | H_0 - \bar{\eta}_0 | \bar{\varphi}_0 \rangle = \bar{G}_0 - \bar{\eta}_0 \equiv 0, \tag{D6a}$$

$$\bar{\Delta}_1 = \langle \bar{\varphi}_0 | H_0 - \bar{\eta}_0 | \bar{\varphi}_1 \rangle + \langle \bar{\varphi}_1 | H_0 - \bar{\eta}_0 | \bar{\varphi}_0 \rangle = \bar{G}_1 = 0, \tag{D6b}$$

$$\begin{aligned} \bar{\Delta}_2 = {} & \langle \bar{\varphi}_0 | H_0 - \bar{\eta}_0 | \bar{\varphi}_2 \rangle + \langle \bar{\varphi}_1 | H_0 - \bar{\eta}_0 | \bar{\varphi}_1 \rangle \\ & + \langle \bar{\varphi}_2 | H_0 - \bar{\eta}_0 | \bar{\varphi}_0 \rangle + \langle \bar{\varphi}_1 | H_1 - \bar{\eta}_1 | \bar{\varphi}_0 \rangle \\ & = \bar{G}_2 + \tfrac{1}{2}\bar{g}_1 = 0, \end{aligned} \tag{D6c}$$

but, in general,

$$\bar{\Delta}_m = \bar{\eta}_m - \left[\langle \bar{\varphi}_0 | H_1 | \bar{\varphi}_{m-1} \rangle - \sum_{r=1}^{m-1} \bar{\eta}_r \langle \bar{\varphi}_0 | \bar{\varphi}_{m-r} \rangle \right] \neq 0, \quad m \geq 3. \tag{D6d}$$

In deriving Eqs. (D6), we have made use of the matrix-element formulation of the G_m and g_{m-1} and of the orthonormality conditions, Eqs. (17) and (18), as well as of Eqs. (16). Equation (D6a) vanishes identically while Eqs. (D6b) and (D6c) vanish because of Eq. (C5) of Appendix C. Thus, for all optimum variational wave functions which satisfy the variational Hellmann-Feynman theorem, $\bar{\Delta}$ vanishes in general only through second order. Since $\langle \bar{\varphi}_0 | \bar{\varphi} \rangle = 1 + O(\lambda^2)$, it follows that the corresponding variational energy shift $(\bar{\eta} - \bar{\eta}_0)$ is *not* given by the equivalent of Eq. (D4) but rather by

$$\bar{\eta} - \bar{\eta}_0 = \langle \bar{\varphi} | H | \bar{\varphi} \rangle - \langle \bar{\varphi}_0 | H_0 | \bar{\varphi}_0 \rangle, \tag{D7a}$$

where

$$(\bar{\eta} - \bar{\eta}_0) - \frac{\langle \bar{\varphi}_0 | H_1 | \bar{\varphi} \rangle \lambda}{\langle \bar{\varphi}_0 | \bar{\varphi} \rangle} = O(\lambda^3), \tag{D7b}$$

a rigorous result. We term Eq. (D7b) the *variational* integral Hellmann-Feynman theorem; a clear statement of this theorem in terms of a well-defined perturbation parameter does not appear to have been previously presented.

Parr[47] has suggested that the approximate expression (correct through second order) for the *variational* energy shift $(\bar{\eta} - \bar{\eta}_0)$

$$\bar{\eta} - \bar{\eta}_0 \approx \frac{\langle \bar{\varphi}_0 | H_1 | \bar{\varphi} \rangle \lambda}{\langle \bar{\varphi}_0 | \bar{\varphi} \rangle} \tag{D8}$$

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[45] A. Fröman, Phys. Rev. 112, 870 (1958).

[46] G. Breit, Rev. Mod. Phys. 23, 238 (1951).

[47] R. G. Parr, J. Chem. Phys. 40, 3726 (1964); H. J. Kim and R. G. Parr, *ibid.* 41, 2892 (1964).

[48] J. W. Richardson and A. K. Pack, J. Chem. Phys. 41, 897 (1964).

may serve as a useful approximation to the *exact* energy shift $(\epsilon-\epsilon_0)$ resulting from changes in molecular conformation.[49] It is appropriate, then, to determine under what circumstances the PV expansion of Eq. (D8) would agree through a given order with the RS expansion of the exact shift

$$\epsilon-\epsilon_0=\sum_{p=1}^{\infty}\epsilon_p\lambda^p. \tag{D9}$$

We recognize the expression in square brackets on the right-hand side of Eq. (D6d) as being identical in form to the familiar expression for the mth-order RS energy expansion term ϵ_m obtained by multiplying the mth-order coupled differential equation of RS perturbation theory[15] from the left by ψ_0^* and integrating. Therefore, a sufficient condition for $\bar{\Delta}$ to vanish through mth order, and hence for Eqs. (D8) and (D9) to agree through mth order, is for the expansions of $\bar{\varphi}$ and ψ to agree through the $(m-1)$th order. On the other hand, as shown in Sec. III and elsewhere,[3,15] if the expansions of $\bar{\varphi}$ and ψ should agree through the $(m-1)$th order, the PV expansion of $\bar{\eta}$ computed directly from $\langle\bar{\varphi}|H|\bar{\varphi}\rangle$ would agree with the RS expansion of ϵ through the $(2m-1)$th order. Thus, the use of Eq. (D8) rather than directly taking the difference of $\bar{\eta}$ and $\bar{\eta}_0$, as in Eq. (D7a), would effectively result in the loss of the $(m-1)$ orders of ϵ_p for $m+1\leq p\leq 2m-1$, and their replacement by approximations; this conclusion is one order less pessimistic than that previously advanced by Musher.[50]

The accuracy with which Eq. (D9) is reproduced by Eq. (D8) can also be discussed in terms of the PV classification of variational wave functions: Category I wave functions satisfying only Eqs. (31) yield results correct through first order; category I wave functions satisfying both Eq. (31) and (36) yield results correct through second order, etc.; all category II and category III wave functions yield results incorrect in all orders. It is apparent that there is nothing to be gained, and much to be lost, if Parr's theorem, Eq. (D8), is applied to accurate (through first- or higher-order) category I wave functions. In practice, however, only relatively poor category II wave functions are presently available for molecular calculations. Although Eq. (D8) is not protected by the variational principle, it is also not restricted by it. Thus, the possibility exists that the use of Eq. (D8) may introduce some compensatory error in the higher-order terms of $\bar{\eta}$ and thereby yield a better approximation to the exact $(\epsilon-\epsilon_0)$ than does the use of the rigorous expression for $(\bar{\eta}-\bar{\eta}_0)$, Eq. (D7a). It is significant to note that since Eqs. (D7a) and (D8) agree through second order in λ, any compensatory error introduced by Eq. (D8) should only become appreciable for rather large λ, i.e., precisely in the range of increasing perturbation where the directly computed $\bar{\eta}$ would be expected to become increasingly inaccurate. This prediction is in accord with the trend of the data reported by Hayes and Parr,[51] who applied Eqs. (D7a) and (D8) to variational wave functions for the HeH^+ molecule; here, λ may be regarded as the inverse nuclear separation.

APPENDIX E: THE VIRIAL THEOREM

The relationship between the virial theorem and the PV procedure is of sufficient interest to warrant detailed analysis elsewhere.[13] Here, only those results are summarized which are relevant to this unified presentation.

Consider a bound system of charged particles interacting with Coulombic forces. Then, the Hamiltonian can be written as

$$H=T+V, \tag{E1}$$

where T and V are, respectively, the kinetic and potential energy operators. Further, in analogy with our treatment of H, Eqs. (2), assume that $V=V(\lambda)$. Then, for $\lambda=0$, the unperturbed Hamiltonian assumes the form

$$H_0=T+V_0, \tag{E2}$$

where V_0 is the unperturbed potential operator. For H given by Eq. (2a), we obtain from Eqs. (E1) and (E2)

$$V=V_0+H_1\lambda. \tag{E3}$$

For such a system, the virial theorem[27] states that for the exact normalized wave function,

$$2\langle\psi|T|\psi\rangle+\langle\psi|V|\psi\rangle=0. \tag{E4}$$

In general, Eq. (E4) is not satisfied if ψ is replaced by an arbitrary variational wave function, whether optimized or not. If, however, the coordinates of each particle in φ are transformed from $\mathbf{R}_i$ to $k\mathbf{R}_i$, where k is a so-called scaling parameter, it is well known[27] that the transformed φ satisfies the virial theorem for the energetically optimized $\bar{k}$. Let us now specify that one of the a_μ contained in the φ of Eq. (3) is such a scaling parameter. Then, for optimum $\bar{\varphi}$,

$$2\langle\bar{T}\rangle+\langle\bar{V}\rangle=0. \tag{E5}$$

Equation (E5) can be expanded in the usual manner by the variational wave-operator formalism or by substituting the PV expansion of the optimum $\bar{\varphi}$, Eq. (9b). This yields for the PV expansion terms

$$2\langle\bar{T}\rangle_0+\langle\bar{V}_0\rangle_0=0, \tag{E6a}$$

and

$$2\langle\bar{T}\rangle_m+\langle\bar{V}_0\rangle_m+\langle\bar{H}_1\rangle_{m-1}=0,\quad m\geq1, \tag{E6b}$$

i.e., the virial theorem is fulfilled in each expansion order. In addition, since

$$\bar{\eta}=\langle\bar{H}\rangle=\langle\bar{T}\rangle+\langle\bar{V}\rangle, \tag{E7}$$

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[49] R. E. Wyatt and R. G. Parr, J. Chem. Phys. 43, S217 (1965); 44, 1529 (1966).

[50] J. I. Musher, J. Chem. Phys. 43, 2145 (1965).

[51] E. F. Hayes and R. G. Parr, J. Chem. Phys. 44, 4650 (1966).

it follows from Eq. (E5) that

$$\bar{\eta} = -\langle \bar{T} \rangle, \tag{E8}$$

with the PV expansion,

$$\bar{\eta}_m = -\langle \bar{T} \rangle_m, \quad m \geq 0; \tag{E9}$$

also

$$\bar{\eta} = \tfrac{1}{2}\langle \bar{V} \rangle, \tag{E10}$$

with the PV expansion,

$$\bar{\eta}_0 = \tfrac{1}{2}\langle \bar{V}_0 \rangle_0, \tag{E11a}$$

and

$$\bar{\eta}_m = \tfrac{1}{2}[\langle \bar{V}_0 \rangle_m + \langle \bar{H}_1 \rangle_{m-1}], \quad m \geq 1. \tag{E11b}$$

Thus, all orders of the PV expansion of the optimum $\bar{\eta}$ can be computed either solely in terms of the kinetic energy operator or of the potential energy operator. Since the exact ψ and ϵ satisfy the virial theorem, Eqs. (E6)–(E11) necessarily also apply to the RS perturbation expansions.[15,20,27]

APPENDIX F: THE SEPARATION OF $\langle \bar{V}_0 \rangle$

It is possible to combine the variational Hellmann-Feynman theorem, Appendix C, and the virial theorem, Appendix E, to obtain another theorem relating to the energetically optimized expectation value of the V_0 operator. In general, from Eqs. (17) and (E2),

$$\bar{G}_m \equiv \langle \bar{H}_0 \rangle_m = \langle \bar{T} \rangle_m + \langle \bar{V}_0 \rangle_m, \tag{F1}$$

so it follows immediately from Eqs. (C6) and (E9) that

$$(2-m)\bar{\eta}_m = \langle \bar{V}_0 \rangle_m, \quad m \geq 0 \tag{F2}$$

for all *scaled, fully optimized* variational wave functions. Thus, all orders of the PV expansion of the optimum $\bar{\eta}$, excepting $\bar{\eta}_2$, can be computed solely in terms of the unperturbed potential operator. Since the exact ψ and ϵ satisfy both the Hellmann-Feynman and the virial theorems, the RS perturbation expansions must also satisfy Eq. (F2); this relation for the exact quantities has previously been derived independently by Fröman,[45] Hall,[32] and Scherr and Knight,[16] and has been discussed by Löwdin.[27] Hall[32] has also discussed the applicability of the theorem to certain approximate wave functions. For an N-electron atomic isoelectronic sequence, the nonrelativistic V_0 operator, in modified atomic units,[1] is given by

$$V_0 = -\sum_{i=1}^{N} R_i^{-1}, \tag{F3}$$

where R_i is the radial coordinate[28] of the ith electron. Then, from Eqs. (F2) and (F3), the PV expansion of $\langle \bar{R}^{-1} \rangle$ in modified atomic units is

$$\langle \bar{R}^{-1} \rangle = \langle \sum_{i=1}^{N} \bar{R}_i^{-1} \rangle = \sum_{m=0}^{\infty} (m-2)\bar{\eta}_m \lambda^m. \tag{F4}$$

APPENDIX G: THE ANOMALOUS PV EXPANSIONS OF SOME OPEN-SHELL ORBITALS

For the ^1S ground state of the He isoelectronic sequence, the open-shell[34] wave function has the general form

$$\varphi = M[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)], \tag{G1}$$

where the separable, antisymmetric spin function has been omitted; here, M is an over-all normalization factor, and φ_a and φ_b are nonequivalent, normalized, s-type variational orbitals. In the analytic, open-shell wave function considered here, the orbitals are taken[4,52] as

$$\varphi_a(i) = (a^3/\pi)^{1/2}\, e^{-aR_i}, \quad \varphi_b(i) = (b^3/\pi)^{1/2}\, e^{-bR_i}, \tag{G2}$$

where the orbital exponents, a and b, are variationally determined. The orbital exponents can also be expressed[4,52] in terms of a scaling parameter k and a splitting parameter x by the transformation

$$a = k(1+x), \quad b = k(1-x). \tag{G3}$$

If x is not allowed to vary freely but is arbitrarily fixed at zero, then

$$\varphi_a = \varphi_b = \varphi_k, \tag{G4}$$

and φ becomes a closed-shell function. With the choice of the open-shell orbitals of Eqs. (G2), it follows from Eqs. (G1) and (G3) that φ is an even function of x,

$$\varphi(k,x) = \varphi(k,-x), \tag{G5}$$

so that, correspondingly, the energy η must also be an even function of x. In particular, it is found[4,52] that

$$\eta = \eta(k,y), \tag{G6}$$

where

$$y = x^2, \tag{G7}$$

and the optimization of η is to be performed in respect to k and y. Then, in PV notation, the unoptimized zero-order energy is

$$\eta_0 = G(k_0, y_0). \tag{G8}$$

In the hydrogenic RS perturbation expansion,[2] the exact zero-order function ψ_0 is given by the closed-shell function

$$\psi_0 = \psi_0^{(H)}(1)\psi_0^{(H)}(2); \tag{G9}$$

here, the $\psi_0^{(H)}(i)$ are normalized hydrogenic $1s$ orbitals with the form

$$\psi_0^{(H)}(i) = (1/\pi)^{1/2}\, e^{-R_i}, \tag{G10}$$

in modified atomic units.[1,28]

From comparison of φ and ψ_0, it is apparent that φ

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[52] H. Shull and P.-O. Löwdin, J. Chem. Phys. 25, 1035 (1956); see also R. P. Hurst, J. D. Gray, G. H. Brigman, and F. A. Matsen, Mol. Phys. 1, 189 (1958).

is a category I wave function, where

$$\bar{k}_0=1, \tag{G11a}$$

$$\bar{y}_0=\bar{x}_0^2=0, \tag{G11b}$$

$$\bar{M}_0=\tfrac{1}{2}, \tag{G11c}$$

$$\bar{\varphi}_{a0}=\bar{\varphi}_{b0}=\bar{\varphi}_{k0}=\psi_0^{(H)}, \tag{G11d}$$

$$\bar{\varphi}_0=\psi_0, \tag{G11e}$$

and

$$\bar{\eta}_0=\epsilon_0=-1. \tag{G11f}$$

Equations (G11) could also have been derived by direct optimization of η_0, Eq. (G8). These results show that $\bar{k}$ is a type-$\bar{b}_\pi$ parameter but $\bar{y}$ is a type-$\bar{c}_\rho$ parameter with the expansion

$$\bar{y}=\sum_{j=1}^{\infty}\bar{y}_j\lambda^j=\bar{y}_1\lambda\Big[1+\sum_{j=1}^{\infty}(\bar{y}_{j+1}/\bar{y}_1)\lambda^j\Big]. \tag{G12}$$

It is apparent from Eq. (G11b) that it is not possible to expand $(\bar{y})^{1/2}$ about $\bar{y}_0$ is a normal PV expansion. From Eq. (G12), however, we obtain

$$(\bar{y})^{1/2}=(\bar{x}^2)^{1/2}=(\bar{y}_1)^{1/2}\lambda^{1/2}\times[1+(\bar{y}_2/2\bar{y}_1)\lambda+O(\lambda^2)], \tag{G13}$$

providing the expansion exists. Since $\bar{k}$ has a normal PV expansion, it follows from Eqs. (G3) and (G13) that

$$\bar{a}=\sum_{j=0}^{\infty}\bar{a}_j\kappa^j,\quad \bar{b}=\sum_{j=0}^{\infty}\bar{b}_j\kappa^j, \tag{G14a}$$

where

$$\kappa=\lambda^{1/2}=Z^{-1/2}, \tag{G14b}$$

in agreement with the observed[4,12] behavior; the expansions of Eqs. (G14) are to be multipled by Z to convert to Hartree atomic units.[1,28] It is not difficult to show that both $\bar{\varphi}$ and $\bar{\eta}$ have normal PV expansions despite the anomalous expansions of $\bar{a}$ and $\bar{b}$, and hence, of $\bar{\varphi}_a$ and $\bar{\varphi}_b$.

These anomalous results are directly dependent upon φ being a category I wave function. Suppose that another choice of orbitals, such as Gaussian,[12] were made for φ_a and φ_b, with the orbital exponents defined as in Eqs. (G3). The resulting φ would necessarily belong to category II. Equations (G4)–(G8) would still be applicable but, in general, the variationally determined optimum value of $\bar{y}_0$ would not vanish. Then, for $\bar{y}_0=\bar{x}_0^2\neq 0$, it is anticipated that $(\bar{y})^{1/2}$, and hence, $\bar{a}$, $\bar{b}$, $\bar{\varphi}_a$, and $\bar{\varphi}_b$ would all have normal PV expansions, again in agreement with the observed behavior[12] for such a wave function.

This method of analysis can readily be generalized as follows: Let the normalized φ_a and φ_b be transformed to

$$\varphi_a=\varphi_k+\varphi_x,\quad \varphi_b=\varphi_k-\varphi_x, \tag{G15}$$

where φ_x is a generalized splitting orbital. Here, the orbitals φ_k and φ_x are defined by the inverse transformation

$$\varphi_k=\tfrac{1}{2}(\varphi_a+\varphi_b),\quad \varphi_x=\tfrac{1}{2}(\varphi_a-\varphi_b), \tag{G16}$$

and are *not* individually normalized. As in the special case treated above, it follows that both φ and η are even functions of φ_x. In particular, η_0 contains terms of the type $\langle\varphi_{x0}|H_0|\varphi_{x0}\rangle$ and $\langle\varphi_{x0}|\varphi_{x0}\rangle$. If φ_a and φ_b are so selected that the conditions of Eq. (G11d) are satisfied, then φ is a category I wave function, where, necessarily,

$$\langle\bar{\varphi}_{x0}|\bar{\varphi}_{x0}\rangle=0, \tag{G17}$$

in analogy with Eq. (G11b). For such functions, it follows that $\bar{\varphi}_x$ has a PV expansion analogous to $(\bar{y})^{1/2}$, Eq. (G13), and $\bar{\varphi}_a$ and $\bar{\varphi}_b$ have expansions analogous to Eq. (G14); this behavior has been observed[35] for the general case of the category I wave function constructed with open-shell, Hartree-Fock orbitals. On the other hand, if φ_a and φ_b are so selected that φ belongs to category II rather than to category I, the conditions of Eq. (G11d) are not fulfilled, and, in general,

$$\langle\bar{\varphi}_{x0}|\bar{\varphi}_{x0}\rangle\neq 0. \tag{G18}$$

For such functions, it is anticipated that $\bar{\varphi}_x$, and hence, $\bar{\varphi}_a$ and $\bar{\varphi}_b$ would have normal PV expansions.