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Generalized Perturbation Method Employing Nonorthogonal Functions*

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A method is developed for solving second-order perturbation problems without explicit knowledge of the higher molecular states. This method involves, in principle, a transformation of basis from the set of ortho-normalized eigenfunctions of the unperturbed molecular Hamiltonian to an arbitrary set of functions not, in general, either normalized or mutually orthogonal, but of such symmetry that perturbation matrix elements connecting them to the ground state do not vanish. If the new basis is chosen expediently, convergence to second-order eigenvalues may be attained with a small number of functions. The method is related to the conventional perturbation and variational approaches. As an illustration, the perturbed harmonic oscillator is treated.

I. INTRODUCTION

WE suppose the eigenvalue problem,

$$\{\mathcal{H}_0 - E^{(0)}\}\psi^{(0)} = 0, \qquad (1)$$

to have been solved exactly for some particular state of a system. We further suppose that the system is subjected to a small perturbation such that

$$\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{V}, \qquad (2)$$

and we wish now to compute the energy of the corresponding state.

Calculation of first-order eigenvalues requires only that we know $\psi^{(0)}$. Second-order contributions, however, require knowledge of eigenfunctions of other states of the unperturbed system. In molecular problems these would include formally all the discrete as well as the continuum solutions of the appropriate Schroedinger equation.[1] Dissociated states of the molecule might also contribute. Since these required eigenfunctions are little known and less tractable, even for the simplest of molecules, unmodified second-order perturbation theory is not effectively applicable, unless it can be shown that only a small number of states contribute to the perturbation.

We propose below a method in which functions more convenient than the eigenfunctions of $\mathcal{H}_0$ can be used in the calculation of second-order eigenvalues. The idea of using such a set of functions was due originally to Epstein.[2] His approach involved, in principle, diag-

onalization of the complete Hamiltonian in a suitable orthonormal basis not necessarily related to the unperturbed system. He applied his method to an accurate computation of the Stark effect in atomic hydrogen. Similar methods have been used by others in the solution of various molecular problems.[3] The extension we propose is the removal of the restriction that the basis be orthonormalized. This formalism has been developed specifically in connection with two problems involving perturbations on molecular hydrogen: the electric dipole moment of HD‡ and the nuclear spin interaction in HD.§ In these computations, we have employed basis functions of the form,

$$(1/2\pi)\exp[-\delta(\lambda_1+\lambda_2)](\lambda_1{}^M\lambda_2{}^N\mu_1{}^J\mu_2{}^K\rho^P$$
$$\pm\lambda_1{}^N\lambda_2{}^M\mu_1{}^K\mu_2{}^J\rho^P), \qquad (3)$$

first used by James and Coolidge[4] and by Present[5] in their studies of the ground and excited states of H_2. These functions form a complete, though not ortho-normal, set. In order to make use of them and of various matrix elements computed by the above authors we have extended the generalized perturbation method of Epstein.[2] We present the method apart from its applications, since it is perhaps of interest in itself.

II. DERIVATION OF THE GENERALIZED PERTURBATION FORMULA

We seek a solution for the perturbed problem,

$$(\mathcal{H} - E)\psi = 0, \qquad (4)$$

by developing ψ linearly as follows‖:

$$\psi = \psi^{(0)} + \sum_n{}' c_n \phi_n, \qquad (5)$$

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[1] The importance of the continuum in atomic problems has most recently been pointed out by: Green *et al.*, Phys. Rev. **96**, 319 (1954); H. Shull and P.-O. Löwdin, J. Chem. Phys. **23**, 1362 (1955); **30**, 617 (1959). In the last reference, Shull and Löwdin estimate that the 2s orbital function in helium contains about 43% continuum character with reference to discrete hydrogen-like functions.
[2] P. S. Epstein, Phys. Rev. **28**, 695 (1926). We are indebted to Professor E. B. Wilson for bringing this reference to our attention. The method is discussed in detail also in L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 190.

[3] J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A129**, 598 (1930); E. Hylleraas, Z. Physik **65**, 209 (1930); H. R. Hassé, Proc. Cambridge Phil. Soc. **26**, 542 (1930); J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).
‡ S. M. Blinder, J. Chem. Phys. **32**, 105 (1960). This work was reported at the Symposium on Molecular Spectroscopy, Ohio State University, June 15–19, 1959.
§ To be published in J. Chem. Phys.
[4] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).
[5] R. D. Present, J. Chem. Phys. **3**, 122 (1935).
‖ We shall use throughout the convention that a prime on the summation sign indicates exclusion of the index 0.

where the $\phi_n (n = 1, \cdots, N)$ represent a set of functions orthogonal to $\psi^{(0)}$ but not necessarily normalized, mutually orthogonal, or solutions of the unperturbed problem.¶ We assume the set $\psi^{(0)}, \phi_1, \cdots, \phi_N$ (where N may be ∞) to be complete in the domain of ψ. In practice, it need be only as nearly complete as the degree of accuracy requires. $\psi^{(0)}$, the normalized solution to Eq. (1), is, of course, a close approximation to ψ, presuming the perturbation to be small.

Substituting our linear development for ψ in Eq. (4) we find

$$(\mathcal{3C} - E)\psi^{(0)} + \sum_n{}'c_n(\mathcal{3C} - E)\phi_n = 0. \tag{6}$$

Multiplying on the left by $\psi^{(0)*}$ and integrating, we obtain

$$E = H_{00} + \sum_n{}'H_{0n}c_n. \tag{7}$$

Similarly, multiplication by $\phi_k{}^*$ yields

$$H_{k0} + \sum_n{}'(H - E)_{kn}c_n = 0. \tag{8}$$

We have employed the notation

$$\left. \begin{array}{c} H_{0n} = \int dq\psi^{(0)*}\mathcal{3C}\phi_n, \quad \text{etc.,} \\[2em] (H - E)_{kn} = \int dq\phi_k{}^*\mathcal{3C}\phi_n - E\int dq\phi_k{}^*\phi_n \end{array} \right\}. \tag{9}$$

Next we multiply Eq. (8) by $[(H - E)^{-1}]_{jk}$ and sum over the index k,** so that

$$\sum_k [(H - E)^{-1}]_{jk}H_{k0}$$
$$+ \sum_k\sum_n{}'[(H - E)^{-1}]_{jk}(H - E)_{kn}c_n = 0. \tag{10}$$

Since

$$\sum_k [(H - E)^{-1}]_{jk}(H - E)_{kn} = \delta_{jn},$$

we find

$$c_j = -\sum_k{}'[(H - E)^{-1}]_{jk}H_{k0}. \tag{11}$$

Applying Eq. (11) to Eq. (7),

$$E - H_{00} - \sum_{n,k}{}''H_{0n}[(H - E)^{-1}]_{nk}H_{k0}. \tag{12}$$

Now we make use of the perturbation assumption, Eq. (2), and separate Eq. (12) into terms of various order. The energy of a perturbed system may be expanded as a power series in the parameter λ,

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots, \tag{13}$$

¶ We have placed the restriction on our basis that the first function be a solution to the unperturbed problem. This is not required by Epstein, reference 2.

** In this paper we use the notation $(A^{-1})_{jk}$ to indicate the inverse of the matrix representing the operator A. When we are dealing with a nonorthogonal basis this is not, in general, identical with the matrix of the inverse operator A^{-1}.

and all we need know of the development of $(H - E)^{-1}$ is that

$$[(H - E)^{-1}]_{nk} = [(H^{(0)} - E^{(0)})^{-1}]_{nk}\{1 + 0(\lambda) + \cdots\}. \tag{14}$$

Denoting the matrix elements of $\mathcal{3C}_0$ and $\mathcal{U}$ in analogous fashion with Eq. (9) and noting that

$$H_{0n}{}^{(0)} = H_{n0}{}^{(0)} = 0 \tag{15}$$

because of the assumed orthogonality of $\psi^{(0)}$ on the ϕ_n, we may write Eq. (12) through terms of second-order in λ as

$$H_{00}{}^{(0)} + \lambda V_{00} - \lambda^2\sum_{nk}{}''V_{0n}[(H^{(0)} - E^{(0)})^{-1}]_{nk}V_{k0}. \tag{16}$$

The summation contributes no other terms of first- or second-order by virtue of Eq. (15).

If we employ the notation

$$\mathcal{R} \equiv \mathcal{3C}_0 - E^{(0)}, \tag{17}$$

we may write finally for the second-order energy[6]

$$E^{(2)} = -\sum_{nk}{}''V_{0n}(R^{-1})_{nk}V_{k0}. \tag{18}$$

Formally, all we require to find the second-order eigenvalue are the perturbation matrix elements connecting $\psi^{(0)}$ with each of the basis functions ϕ_n and the $\mathcal{R}$ matrix elements between all pairs of such functions. The set $\{\phi_n\}$ need, of course, include only functions of such symmetry that the V_{0n} do not vanish identically. We observe that nowhere, as required by conventional perturbation theory, need we know anything of the structure of any state of the system other than the one in question.

III. CONNECTION WITH CONVENTIONAL PERTURBATION THEORY

Since the domain of ψ may be spanned by an infinite number of complete sets of functions, any two of which are connected by some linear transformation, we can, in principle, regard Eq. (18) as the result of a change in basis from the set of eigenvalues of the unperturbed Hamiltonian to the set $\{\phi_n\}$. (We write $\psi^{(0)}$ alternatively as ϕ_0, and regard it as a member of $\{\phi_n\}$ also.) In particular, we shall now show that if $\psi_k{}^{(0)}(k = 0, 1, \cdots, N)$ represent orthonormalized eigenfunctions of $\mathcal{3C}_0$, then the usual equation,

$$E_0{}^{(2)} = -\sum_k{}'\frac{v_{0k}v_{k0}}{E_k{}^{(0)} - E_0{}^{(0)}} \tag{19}$$

for the second-order energy of the state labeled by subscript 0 reduces to Eq. (18); if the $\psi_k{}^{(0)}$ are linearly

[6] This expression is somewhat similar to one derived by Shull and Simpson, J. Chem. Phys. **28**, 925 (1958), for a consolidated variation-perturbation approach. They use orthonormal functions, however.

dependent on the ϕ_n,

$$\psi_k^{(0)} = \sum_n c_{kn}\phi_n. \qquad (20)$$

Note that this is not, in general, a unitary transformation since the orthonormality of the set $\{\phi_n\}$ is not required. Matrix elements with respect to the orthonormal basis are written in lower case.

The matrix r_{kl} is, by virtue of the orthonormality of the $\psi_k^{(0)}$, of diagonal form,

$$r_{kl} = (E_k^{(0)} - E_0^{(0)})\delta_{kl}. \qquad (21)$$

Furthermore,

$$(r^{-1})_{kl} = (r_{kl})^{-1} = \frac{\delta_{kl}}{E_k^{(0)} - E_0^{(0)}}. \qquad (22)$$

Multiplying by v_{l0} and summing over the index l we obtain

$$\sum_l{}' (r^{-1})_{kl}v_{l0} = \sum_l{}' \frac{\delta_{kl}v_{l0}}{E_k^{(0)} - E_0^{(0)}} = \frac{v_{k0}}{E_k^{(0)} - E_0^{(0)}}; \qquad (23)$$

Eq. (19) may be written in a form analogous to Eq. (18), and

$$E_0^{(2)} = -\sum_{kl}{}'' v_{0k}(r^{-1})_{kl}v_{l0}. \qquad (24)$$

We need only show now that this form is invariant under the transformation in Eq. (20).

Matrix elements in the two representations are related by

$$\left.\begin{aligned} v_{0k} &= \sum_n c_{kn}V_{0n}, \\[1mm] v_{l0} &= \sum_m c_{lm}{}^* V_{m0}, \end{aligned}\right\} \qquad (25)$$

and,

$$r_{kl} = \sum_{sr} c_{ks}{}^* R_{sr} c_{lr}. \qquad (26)$$

The inverse of Eq. (26) is given by

$$(r^{-1})_{kl} = \sum_{sr} (c^{-1})_{sk}(R^{-1})_{sr}(c^{-1})_{rl}{}^*. \qquad (27)$$

Substituting Eqs. (25) and (27) into Eq. (24) and summing over indices k, l we obtain Eq. (18). Conversely, it is easily shown by an analogous procedure that Eq. (18) becomes Eq. (19) when the ϕ_n are linearly dependent on the $\psi_k^{(0)}$.

IV. RELATION TO THE VARIATIONAL METHOD

It is instructive to consider also an alternative derivation of Eq. (18) from the standpoint of the variational principle. We begin, as before, with a linear development for ψ

$$\psi = \psi^{(0)} + \sum_{n=1}^{N} c_n\phi_n, \qquad (28)$$

but recognize, however, the fact that the set $\{\phi_n\}$ in practice is but a small finite one and nowhere near

complete. Consistent with this, we shall attempt to find the best second-order energy, determining the c_n by the variational principle.

For an arbitrary trial function χ of suitable symmetry characteristics,

$$\mathfrak{F}(\chi) = \int dq \chi^* \mathfrak{K}\chi - E \int dq \chi^* \chi \geq 0, \qquad (29)$$

where E is the eigenvalue for the perturbed problem; the lowest one, in the event the original state is degenerate. Should the exact solution of the Schroedinger equation, Eq. (4), be substituted for χ, $\mathfrak{F}$ would vanish and moreover assume a stationary value with respect to all parameters in χ.

Our procedure shall be to substitute our linear development of ψ for χ and minimize $\mathfrak{F}$ with respect to the c_n. The inequality in Eq. (29) will then delimit the value for E. By using Eq. (28) in Eq. (29),

$$\mathfrak{F}(c_1, \cdots, c_N) = \begin{cases} H_{00} - E + \sum_n{}' (c_n{}^* H_{n0} + H_{0n}c_n) \\[2mm] + \sum_{mn}{}'' c_n{}^* c_m (H_{nm} - E S_{nm}), \end{cases} \qquad (30)$$

where we have defined

$$S_{nm} \equiv \int dq \phi_n{}^* \phi_m,$$

and noted the orthogonality of the ϕ_m to $\psi^{(0)}$. We apply now the usual power series expansions in the perturbation parameter λ,

$$\left.\begin{aligned} H_{ij} &= H_{ij}^{(0)} + \lambda V_{ij}, \\[1mm] c_n &= \lambda c_n^{(1)} + \lambda^2 c_n^{(2)} + \cdots \end{aligned}\right\}. \qquad (31)$$

Substituting Eqs. (13), (15), (17), and (31) into Eq. (30), and recalling that $H_{00}^{(0)} = E^{(0)}$ and $V_{00} = E^{(1)}$, we obtain, to terms of second order in λ,

$$\mathfrak{F}(c_1, \cdots, c_N) = \begin{cases} \lambda^2 \{ -E^{(2)} + \sum_n{}' (c_n{}^* V_{n0} + V_{0n}c_n) \\[2mm] + \sum_{mn}{}'' c_n{}^* c_m R_{nm} \} + 0(\lambda^3). \end{cases} \qquad (32)$$

We now apply the variational conditions

$$\partial\mathfrak{F}/\partial c_k = 0, \qquad k = 1, \cdots, N, \qquad (33)$$

obtaining the set of equations

$$V_{0k} + \sum_n{}' c_n{}^* R_{nk} = 0, \qquad k = 1, \cdots, N, \qquad (34)$$

apart from terms of order λ^3. These are equivalent to the set,

$$V_{k0} + \sum_n{}' R_{kn}c_n = 0, \qquad k = 1, \cdots, N, \qquad (35)$$

obtained by minimizing with respect to the $c_k{}^*$. The

nontrivial solutions of Eq. (35) are

$$c_u = -\sum_k{}'(R^{-1})_{nk}V_{k0}, \quad k=1, \cdots, N. \quad (36)$$

Applying the inequality $\mathfrak{F}\geq 0$, we establish finally the equation delimiting the second-order perturbation energy,

$$E^{(2)} \leq -\sum_{nk}{}''V_{0m}(R^{-1})_{nk}V_{k0}, \quad (37)$$

the equality holding only when the set $\{\phi_n\}$ is rigorously complete.

V. DISCUSSION

Little can be said regarding the form of the ϕ_n, or the number of such functions required to approximate $E^{(2)}$ to a given degree of accuracy without reference to some particular problem. A good indication of the relative importance of some ϕ_n may be obtained from its contribution were it the sole perturbing state,

$$E_n^{(2)} = -\mid V_{0n}\mid^2/R_{nn}. \quad (38)$$

Strictly speaking, however, each function must be tested in combination with others before it may be neglected validly. To obtain an idea of how well convergence to the true $E^{(2)}$ is proceeding, one might enlarge the basis by adding some "good" function ϕ_n, i.e., one with relatively large $E_n^{(2)}$. If the resulting change in $E^{(2)}$ is small, the accuracy of $E^{(2)}$ is strongly indicated.

Just as the variational result in Eq. (37) gives an upper bound on the value of $E^{(2)}$, the second-order perturbation in Eq. (19) can provide a lower one if the state labelled by subscript 0 is the ground state. This follows from the inequality,

$$\sum_n{}'[V_{0n}V_{n0}/(E_n-E_0)]\leq[1/(E_1-E_0)]\sum_n{}'V_{0n}V_{n0}$$

$$=[(V^2)_{00}-(V_{00})^2]/(E_1-E_0), \quad (39)$$

where E_1 is the energy of the lowest contributing excited state and

$$(V^2)_{00}=\int dq\psi_0^{(0)}{}^*\mathcal{U}^2\psi_0^{(0)}. \quad (40)$$

Thus

$$E_0^{(2)} = -\sum_n{}'[V_{0n}V_{n0}/(E_n-E_0)]$$

$$\geq -[(V^2)_{00}-(V_{00})^2]/(E_1-E_0), \quad (41)$$

and $E_0^{(2)}$ is bracketed by Eqs. (37) and (41).††

Unless there is good reason to believe that the major constribution to $E^{(2)}$ is from a single state, Eq. (41) can not be regarded too seriously from a quantitative

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†† It should perhaps be noted that the concepts of upper and lower limit are here employed in the algebraic sense. Since, for nondegenerate ground states, second-order perturbation energies are always negative, absolute magnitudes of these quantities must be interpreted in the opposite sense as regards upper and lower limit.

point of view. However, Eq. (41) almost certainly indicates the correct order of magnitude. Furthermore, it may indicate the behavior of a second-order eigenvalue with respect to some parameter.

Next we shall write out Eq. (37) explicitly for the case of two basis functions. Assuming that we have computed the requisite matrix elements, we find

$$E_{1,2}^{(2)} = -\frac{V_{01}^2R_{22}-2V_{01}V_{02}R_{12}+V_{02}^2R_{11}}{R_{11}R_{22}-R_{12}^2}, \quad (42)$$

choosing, for convenience, all matrix elements to be real.

For the case $R_{12}=0$, Eq. (42) reduces to

$$E_{1,2}^{(2)} = -(V_{01}^2/R_{11})-(V_{02}^2/R_{22})=E_1^{(2)}+E_2^{(2)}, \quad (43)$$

using the notation of Eq. (38). Hence we may generalize that when basis functions of different symmetry are involved, the R matrix of each type may be inverted separately, and the energy contributions are additive.

We consider finally the evaluation of second-order properties other than that of the energy. Referring to our original expansion Eqs. (5) or (28), the expectation value of some operator Q for the perturbed state in question is found from

$$\langle Q \rangle = \int dq\psi^*Q\psi \Big/ \int dq\psi^*\psi. \quad (44)$$

Substituting the optimal expansion coefficients from Eq. (36), we find the second-order contribution,

$$Q^{(2)} \approx -\sum_{nk}{}''\{Q_{0n}(R^{-1})_{nk}V_{k0}+V_{0n}(R^{-1})_{nk}Q_{k0}\}. \quad (45)$$

Since no extremum properties hold, in general, for the operator Q, we may state merely that Eq. (45) approximates $Q^{(2)}$ without specification as to whether this is an upper or a lower bound. However, since a function having a more accurate energy eigenvalue generally gives more dependable values for other properties, we may, with little additional labor, compute $E^{(2)}$ also, and observe its convergence properties as a test of our basis.

VI. A SIMPLE APPLICATION: THE PERTURBED HARMONIC OSCILLATOR

As a somewhat trivial though illustrative example of our perturbation method we shall consider the ground state of the harmonic oscillator perturbed by a small cubic potential term.

The Hamiltonian for an unperturbed one-dimensional harmonic oscillator in an appropriately scaled system of units may be written

$$\mathfrak{IC}_0 = -(d^2/dx^2)+x^2. \quad (46)$$

The eigensolutions are[7]

$$\psi_n{}^{(0)} = [\pi^{-1/4}/(2^n n!)^{\frac{1}{2}}] \exp(-x^2/2) H_n(x),$$

$$E_n{}^{(0)} = 2n+1, \quad (47)$$

where $H_n(x)$ is the nth Hermite polynomial. The only states we shall require explicitly are the following:

$$\psi_0{}^{(0)} = \pi^{-1/4} \exp(-x^2/2), \qquad E_0{}^{(0)} = 1;$$

$$\psi_1{}^{(0)} = \pi^{-1/4} 2^{-1/2} x \exp(-x^2/2), \qquad E_1{}^{(0)} = 3;$$

$$\psi_3{}^{(0)} = \pi^{-1/4} 3^{-1/2} (2x^3 - 3x) \exp(-x^2/2), \qquad E_3{}^{(0)} = 7.$$

$$(48)$$

We consider now a cubic anharmonicity, corresponding to a perturbation

$$\mathcal{U} = \kappa x^3, \quad (49)$$

where, in order for perturbation methods to be valid, we require $\kappa \ll 1$.

We compute the energy first by ordinary perturbation theory. This is possible here since only two states perturb the ground state, the first and third excited states, as follows readily from the properties of Hermite polynomials. To compute the necessary matrix elements requires only the integrals

$$\int_{-\infty}^{\infty} dx \exp(-x^2) = \pi^{\frac{1}{2}},$$

$$\int_{-\infty}^{\infty} dx x^{2n} \exp(-x^2) = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)\pi^{\frac{1}{2}}}{2^n}, \quad (50)$$

$$n = 1, 2, \cdots.$$

The perturbation energy to second-order is given by

$$E^{(2)} = -\{[V_{01}{}^2/(E_1 - E_0)] + [V_{03}{}^2/(E_3 - E_0)]\}$$

$$= -\tfrac{11}{16}\kappa^2. \quad (51)$$

For purposes of comparison, we estimate the energy by

TABLE I

$V_{0a} = (3/4)\pi^{1/4}\kappa$	$R_{aa} = \pi^{1/2}$	$R_{ab} = (3/2)\pi^{1/2}$
$V_{0b} = (15/8)\pi^{1/4}\kappa$	$R_{bb} = (27/4)\pi^{1/2}$	$R_{ac} = (15/4)\pi^{1/2}$
$V_{0c} = (105/16)\pi^{1/4}\kappa$	$R_{cc} = (25/16)105\pi^{1/2}$	$R_{bc} = (225/8)\pi^{1/2}$

[7] See, for example, L. Pauling and E. B. Wilson, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), Chap. III.

TABLE II.

$E_{ab}{}^{(2)} = -0.6875\kappa^2[-(11/16)\kappa^2]$	100%
$E_{ac}{}^{(2)} = -0.6563\kappa^2$	95%
$E_a{}^{(2)} = -0.5625\kappa^2[-(9/16)\kappa^2]$	82%
$E_{bc}{}^{(2)} = -0.5542\kappa^2$	81%
$E_b{}^{(2)} = -0.5208\kappa^2$	76%
$E_c{}^{(2)} = -0.2625\kappa^2$	38%

the summation procedure of Eq. (41),

$$E^{(2)} \geq -[(V^2)_{00}/(E_1 - E_0)] = -\tfrac{15}{16}\kappa^2, \quad (52)$$

which is certainly of the correct magnitude.

We proceed now to a computation of $E^{(2)}$ by our method. We use three trial functions:

$$\begin{cases} \phi_a = x \exp(-x^2/2) \\ \phi_b = x^3 \exp(-x^2/2) \\ \phi_c = x^5 \exp(-x^2/2). \end{cases} \quad (53)$$

From symmetry considerations it is evident that only odd functions contribute in second order. We may anticipate immediately that the two-function basis ϕ_a, ϕ_b is equivalent to $\psi_1{}^{(0)}$, $\psi_3{}^{(0)}$, and should immediately yield the correct energy; it will be of interest to observe how closely each one alone predicts $E^{(2)}$, as well as to note the effect of the admittedly extraneous function ϕ_c.

The necessary matrix elements are readily computed using Eq. (50). They appear in Table I. The second-order energy is computed by Eqs. (38) and (42) for all possible one and two-function bases. The results are given in Table II together with the percentage of the correct value, $-\tfrac{11}{16}\kappa^2$. All but $E_c{}^{(2)}$ must be termed respectable results. Evidently, addition of ϕ_c to the basis affords considerable improvement nevertheless.

The foregoing example illustrates that the modified method can be as convenient and as accurate as ordinary perturbation theory, even when the latter is applicable. Moreover, when trial functions are suitably chosen, rapid convergence is obtained.

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