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Multiperturbation approach to potential energy surfaces for polyatomic molecules

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In Z-dependent perturbation theory, the lowest-order wave functions for a polyatomic molecule are not only independent of the nuclear charges, but also of the total number of nuclear centers and electrons in the molecule. The complexity of the problem is then determined by the highest order retained in the calculation. Choosing the simplest possible unperturbed Hamiltonian, we describe an n-electron, m-center polyatomic molecule as n ''hydrogenic'' electrons on a single center perturbed by electron–electron and electron–nucleus Coulomb interactions. With this H_0, the first-order wave function for any polyatomic molecule will be a sum of products of hydrogenic orbitals with either two-electron, one-center or one-electron, two-center first-order wave functions. These first-order wave functions are obtained from calculations on He-like and H_2^+-like systems. Similarly, the nth-order wave function decouples so that the most complex terms are just the nth-order wave functions of all the p-electron, q-center subsystems $(p+q=n+2)$ contained in the molecule. We illustrate applications of this method with some results, complete through third order in the energy, for H_3^+-like molecules. These are compared with accurate variational results available in the literature. We conclude that, through this order, this perturbation approach is capable of yielding results comparable in accuracy to variational calculations of moderate complexity. The ease and efficiency with which such results can be obtained suggests that this method would be useful for generating detailed potential energy surfaces for polyatomic molecules. © *1995 American Institute of Physics.*

I. INTRODUCTION

Z-dependent perturbation theory (ZDPT) has long been a powerful computational tool for atomic systems. Little comparable work has been done, however, in molecular systems. Examples include the work of Goodisman[1] and of Matcha and Byers Brown[2] (on diatomic systems) based on an unperturbed Hamiltonian taken as the sum of one-electron, diatomic (H_2^+-like) Hamiltonians, and the work of Dvorácek and Horák[3] (on the hydrogen molecule), of Chisholm and Lodge,[4] (on two-electron diatomic systems), and of Montgomery, Bruner, and Knight[5] (on ten-electron hydrides), all of which utilize single-center, hydrogenic Hamiltonians to describe the unperturbed system. These approaches illustrate one characteristic of the application of ZDPT to molecules; it is possible to construct a variety of unperturbed Hamiltonians and still retain the essential features of the theory.

The advantages of ZDPT and a multiperturbation approach for atomic systems are discussed in Sanders.[6] The present paper extends this earlier work to polyatomic systems. One of the advantages of ZDPT is its ability to provide results for an entire isoelectronic sequence from a single calculation. While this is less significant for polyatomic systems, where few molecular isoelectronic sequences have more than one or two physically interesting examples, the method retains some important advantages for molecular systems. As usual, the inverse nuclear charge appears as a natural perturbation parameter of the method. In addition, the ratio of the nuclear charges also appears as a natural choice of expansion parameter in a multiple perturbation theory. These ensure a rapid convergence of the multiperturbation series for molecules possessing at least one heavy atom. Of greater importance, with these perturbation parameters the individual multiperturbation wave functions and energy coefficients are independent of the nuclear charges as well as of the total number of electrons and the overall electronic configuration of the system. Consequently, results obtained for small systems can be transferred without modification to larger systems which contain the electron configuration of the smaller system as a subconfiguration. It is these characteristics of the method that suggest that ZDPT can be an accurate and efficient method for studying potential energy surfaces of polyatomic systems.

Chisholm and Lodge[4] studied the ground state of two-electron diatomic systems (specifically H_2 and HeH^+) through second-order in the energy. The present paper extends these calculations to third order in the energy. These results are then incorporated into a study of the H_3^+, HeH_2^{+2} sequence as the simplest prototype of a polyatomic molecule. As in Refs. 3–5, we place all the unperturbed (hydrogenic) orbitals on the same nuclear charge. Of the various possible choices of a zero-order Hamiltonian, this produces the simplest form for the higher-order perturbation coefficients. It

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also means that contributions of the interelectron interaction can be obtained directly from ZDPT calculations for atoms. The complete, first-order wave function of any molecule can then be constructed from the first-order, atomic (He-like) pair functions of all two-electron configurations present in the zero-order wave function, together with the first-order, one-electron diatomic (H_2^+-like) wave functions of all the orbitals in the zero-order wave function. Similarly, the second-order correction to the energy consists entirely of one-center three-electron, two-center two-electron, and three-center one-electron contributions, no matter how complex the molecule. Continuing to higher-order, the maximum degree of complexity of the calculation increases in a predictable manner, with each additional order of the calculation introducing either an additional electron or an additional center to the expansion coefficients.

Despite its simplicity, this zero-order Hamiltonian is clearly not the best choice for many polyatomic molecules, particularly homonuclear molecules. Nevertheless, it will serve here to illustrate the general structure of the multiperturbation expansion and the general characteristics of the method. A more natural choice of zero-order Hamiltonian would distribute the electrons for the system among the nuclear centers. This would significantly improve the initial, unperturbed electron density and hence also improve the convergence of the perturbation series, particularly as one approaches the separated-atom limit. Of course, this would also increase the complexity of the calculation at each order of the perturbation by precisely the number of additional centers that have been introduced into the zero-order Hamiltonian. Such generalizations of the method are straightforward and will be examined in more detail in a later paper.

II. THEORY

We describe an unperturbed N-electron, M-center polyatomic molecule as N ''hydrogenic'' electrons on a single center of charge Z_A. In charge-scaled atomic units,[7] this Hamiltonian is written as $H=H_0+H_1$, where

$$H_0=\sum_{i=1}^{N}\left(-\frac{1}{2}\Delta_i-\frac{1}{r_{iA}}\right), \tag{1}$$

$$H_1=\sum_{i=1}^{N}\left(\sum_{j>i}^{N}\lambda_{ij}H_1^{ij}+\sum_{\alpha=B}^{M}\lambda_{i\alpha}H_1^{i\alpha}\right),$$
$$H_1^{ij}=\frac{1}{r_{ij}},\quad H_1^{i\alpha}=-\frac{1}{r_{i\alpha}}, \tag{2}$$

where $\lambda_{ij}=Z_A^{-1}$ and $\lambda_{i\alpha}=Z_\alpha Z_A^{-1}$; the Z_α being the charges of the other atoms in the molecule. The perturbation expansion coefficients are then independent of the nuclear charges and completely transferable from one system to another. This choice of zero-order Hamiltonian also reduces to a minimum the number of nuclear centers that can appear at any particular order. Note that the ratio of the nuclear charges appears in these perturbation expansions in addition to the usual inverse of the nuclear charge. Obviously, Z_A should be chosen as the largest of the nuclear charges in the molecule, if possible. In any case, it is clear that the convergence of portions of the multiperturbation series will be slower than might be anticipated based on the size of Z_A alone.

Treating each term in Eq. (2) as a separate perturbation, we obtain the multiperturbation differential equations.[6] Through second order, these are

$$G_0\psi_0=0, \tag{3}$$
$$G_0\psi_1^{ij}+G_1^{ij}\psi_0=0, \tag{4}$$
$$G_0\psi_1^{i\alpha}+G_1^{i\alpha}\psi_0=0, \tag{5}$$
$$G_0\psi_2^{ij}+G_1^{ij}\psi_1^{ij}-\epsilon_2^{ij}\psi_0=0, \tag{6}$$
$$G_0\psi_2^{i\alpha}+G_1^{i\alpha}\psi_1^{i\alpha}-\epsilon_2^{i\alpha}\psi_0=0, \tag{7}$$
$$G_0\psi_{1,1}^{ij,jk}+G_1^{ij}\psi_1^{jk}+G_1^{jk}\psi_1^{ij}-\epsilon_{1,1}^{ij,jk}\psi_0=0, \tag{8}$$
$$G_0\psi_{1,1}^{ij,i\alpha}+G_1^{ij}\psi_1^{i\alpha}+G_1^{i\alpha}\psi_1^{ij}-\epsilon_{11}^{ij,i\alpha}\psi_0=0, \tag{9}$$
$$G_0\psi_{1,1}^{i\alpha,i\beta}+G_1^{i\alpha}\psi_1^{i\beta}+G_1^{i\beta}\psi_1^{i\alpha}-\epsilon_{1,1}^{i\alpha,i\beta}\psi_0=0, \tag{10}$$

where $G_0=H_0-\epsilon_0$, and $G_1^a=H_1^a-\epsilon_1^a$. Equations (4) and (6) reduce to two-electron, one-center equations, while Eqs. (5) and (7) simplify to one-electron, two-center equations. Equations (8), (9), and (10) are three-electron one-center, two-electron two-center, and one-electron three-center equations, respectively. From these perturbation differential equations one can obtain all corrections to the energy through fifth order.[8] Expressions for the third-order energy coefficients are presented below. In these expressions, a, b, and c represent any one of the perturbations ij or $i\alpha$, with the restriction that all perturbations appearing in a coefficient must be different:

$$\begin{aligned}
&\epsilon_1^a=\langle\psi_0|H_1^a|\psi_0\rangle,\\
&\epsilon_2^a=\langle\psi_1^a|G_1^a|\psi_0\rangle,\\
&\epsilon_{1,1}^{a,b}=2\langle\psi_1^a|G_1^b|\psi_0\rangle,\\
&\epsilon_3^a=\langle\psi_1^a|G_1^a|\psi_1^a\rangle-2\epsilon_2^a\langle\psi_1^a|\psi_0\rangle,\\
&\epsilon_{2,1}^{a,b}=2\langle\psi_1^a|G_1^a|\psi_1^b\rangle+\langle\psi_1^a|G_1^b|\psi_1^a\rangle-2\epsilon_2^a\langle\psi_1^b|\psi_0\rangle\\
&\qquad-2\epsilon_{1,1}^{a,b}\langle\psi_1^a|\psi_0\rangle,\\
&\epsilon_{1,1,1}^{a,b,c}=2(\langle\psi_1^a|G_1^b|\psi_1^c\rangle+\langle\psi_1^b|G_1^a|\psi_1^c\rangle+\langle\psi_1^a|G_1^c|\psi_1^b\rangle\\
&\qquad-\epsilon_{1,1}^{a,b}\langle\psi_1^c|\psi_0\rangle-\epsilon_{1,1}^{a,c}\langle\psi_1^b|\psi_0\rangle-\epsilon_{1,1}^{b,c}\langle\psi_1^a|\psi_0\rangle).
\end{aligned} \tag{11}$$

Extensions to higher order are straightforward, and examples can be found in Ref. 6.

It can be shown that all ''unlinked'' wave functions decouple into simple products of their ''linked'' components, e.g.,

$$\begin{aligned}
&\psi_{1,1}^{12,34}=\psi_1^{12}\psi_1^{34},\\
&\psi_{1,1}^{1\alpha,2\alpha}=\psi_1^{1\alpha}\psi_1^{2\alpha},\\
&\psi_{1,1,1}^{12,23,4\alpha}=\psi_{1,1}^{12,23}\psi_1^{4\alpha}.
\end{aligned} \tag{12}$$

From this it follows that all such ''unlinked'' energy coefficients disappear, e.g., $\epsilon_{1,1}^{12,3\alpha}=0$. These results ensure that at nth order the wave functions and energy coefficients cannot involve more than p electrons and q centers, where $p+q=n$

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$+2$. This in turn means that an nth order perturbation correction can involve no more than $n+1$ coupled electrons while the greatest number of nuclear centers involved in nth order is also $n+1$.

A. Charge-scaling in molecules

In contrast to the corresponding expressions for atoms, the multiperturbation expansions for a molecule have a much more complex behavior with respect to the nuclear charges. The multiperturbation expansion for the electronic energy of a heteronuclear diatomic molecule serves to illustrate this behavior. In charge-scaled atomic units, this is

$$E=\epsilon_0+\sum_{n=1}\lambda_B^n\epsilon_n^M+Z_A^{-1}\left(\epsilon_1^A+\sum_{n=1}\lambda_B^n\epsilon_{1,n}^{A,M}\right)+Z_A^{-2}\left(\epsilon_2^A+\sum_{n=1}\lambda_B^n\epsilon_{2,n}^{A,M}\right)+Z_A^{-3}\left(\epsilon_3^A+\sum_{n=1}\lambda_B^n\epsilon_{3,n}^{A,M}\right)+\cdots, \tag{13}$$

where $\lambda_B=Z_BZ_A^{-1}$. A comparable expression for the energy of a polyatomic molecule requires a simple and obvious extension of this form and introduces no new behavior with respect to charge-scaling. The notation in Eq. (13) has been simplified so that each ''molecular'' coefficient, ϵ_n^M, each ''atomic'' coefficient, ϵ_n^A, and all ''mixed'' coefficients have implicit in them sums over all N electrons of the molecule. The first two terms in this expression represent the sum of the energies of all states of those one-electron diatomic molecules which are subsystems of the molecule, while the sum over all the first (''atomic'') coefficients in each of the bracketed terms represents the energy of the atom which is a subsystem of the diatomic molecule.

Since $\lambda_B\geqslant Z_A^{-1}$, the convergence of those parts of the series involving λ_B can be slower than that of the purely ''atomic'' contributions. An obvious exception to this occurs for the hydrides, where all the multiperturbation expansion parameters are identically Z_A^{-1}, and the multiperturbation expansion simply becomes a formal device for identifying the contributions from subsystems of the molecule. Perturbation energies and other properties of hydrides will thus have simple charge-scaling behavior. At the other extreme are the homonuclear molecules, for which all $\lambda_B=1$. Here, the results obtained via perturbation theory can be seriously affected by a premature truncation of the perturbation series. Note in particular that the entire portion of the energy arising from purely one-electron diatomic energy coefficients is of the same order (in terms of the nuclear charges) as the zero-order term. Similarly, terms of a particular order in Z_A^{-1} will contain contributions from multiperturbation coefficients of much higher nominal order. Hence, for homonuclear molecules, truncating the perturbation sum at some order can yield a *relative* error which actually increases as Z_A increases. The convergence of the energy can be improved considerably, however, by including the higher-order coefficients of one-electron diatomics. This is effectively what was done in the work of Joulakian[9] on isoelectronic homonuclear diatomics.

Finally, it must be kept in mind that all lengths, including internuclear separations, have been scaled by Z_A. Hence, energies calculated at a particular *scaled* internuclear distance will actually correspond to different internuclear separations for different members of an isoelectronic molecular sequence according to the relation $R(\text{bohr})=Z_A^{-1}\times R(\text{scaled a.u.})$.

B. Degeneracy

In degenerate multiple perturbation theory, the multiperturbation expansion becomes algebraically more complex.[8] Nevertheless, the multiperturbation expansion coefficients can still be constructed from the corresponding coefficients of smaller subsystems of the molecule. Chisholm and Lodge[10] have described one approach to this problem, demonstrating how these perturbation coefficients can be constructed.

For the ground state of two-electron molecules, the zero-order wave function is a product of hydrogenic $1s$ orbitals and is not degenerate. Thus, in what follows, this system will serve to illustrate the structure of the method most clearly and simply. The single-center, zero-order wave functions for excited states of these systems and for the ground state of three-electron molecules will be degenerate, however. To illustrate the application of the method to these more complex, often degenerate systems, a brief discussion of the multiperturbation expressions for H_3-like molecules is presented in the Appendix.

III. APPLICATION TO H_3^+-LIKE MOLECULES

For two-electron, three-center molecules, the complete perturbation is

$$H_1=\frac{1}{Z_A}\left[\frac{1}{r_{12}}-Z_B\left(\frac{1}{r_{1B}}+\frac{1}{r_{2B}}\right)-Z_c\left(\frac{1}{r_{1C}}+\frac{1}{r_{2C}}\right)\right]. \tag{14}$$

For $Z_C=0$, this becomes the perturbation for H_2-like molecules. Hence, in what follows, all expressions are written for H_3^+-like systems, expressions for two-electron diatomics being obtained by simply setting Z_C equal to zero. The complete, first-order energy coefficient for the ground state of the molecule is

$$\epsilon_1=\epsilon_1^{1^1S}+2Z_B\epsilon_1^{1s\sigma}(R_B)+2Z_C\epsilon_1^{1s\sigma}(R_C). \tag{15}$$

Here $\epsilon_1^{1^1S}=\frac{5}{8}$ is the first-order correction to the ground state energy of a two-electron atom (and corresponds to an ϵ_1^{ij}) while

$$\epsilon_1^{1s\sigma}(R)=-\frac{1}{R}+\left(1+\frac{1}{R}\right)e^{-2R} \tag{16}$$

is the first-order correction to the ground state energy of a one-electron diatomic molecule with internuclear distance R (and corresponds to an $\epsilon_1^{i\alpha}$). R_B and R_C are the internuclear distances between the charge Z_A and the two perturbing charges, Z_B and Z_C. The angle subtended by these two charges is denoted by Θ.

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Each term in the perturbation, Eq. (3), yields a corresponding term in the complete first-order wave function

$$\psi_1 = \psi_1^{1^1S}(\mathbf{r}_1,\mathbf{r}_2) + Z_B[\psi_1^{1s\sigma}(R_B,\mathbf{r}_1)1s(\mathbf{r}_2) + 1s(\mathbf{r}_1)\psi_1^{1s\sigma}(R_B,\mathbf{r}_2)] + Z_C[\psi_1^{1s\sigma}(R_C,\mathbf{r}_1)1s(\mathbf{r}_2) + 1s(\mathbf{r}_1)\psi_1^{1s\sigma}(R_C,\mathbf{r}_2)]. \tag{17}$$

$\psi_1^{1^1S}$ can be obtained accurately from variational perturbation calculations[11] while $\psi_1^{1s\sigma}$ can be expressed in closed form in confocal elliptic coordinates,[12] but is here also obtained from a variational perturbation calculation.

With this wave function, the second- and third-order energy coefficients can be calculated. The second-order energy is given by

$$\epsilon_2 = \epsilon_2^{1^1S} + 2Z_B^2\epsilon_2^{1s\sigma}(R_B) + 2Z_C^2\epsilon_2^{1s\sigma}(R_C) + Z_B\epsilon_{1,1}^{1^1S,1s\sigma}(R_B) + Z_C\epsilon_{1,1}^{1^1S,1s\sigma}(R_C) + 2Z_BZ_C\epsilon_{1,1}^{1s\sigma,1s\sigma}(R_B,R_C,\Theta), \tag{18}$$

where $\epsilon_2^{1^1S} = -0.157\ 666\ 4$,[11] $\epsilon_2^{1s\sigma}$ is known exactly,[12] and $\epsilon_{1,1}^{1^1S,1s\sigma}$ is given in Ref. 4. Note that the dependence of the *electronic* energy on the angle Θ makes its first appearance at this order through the three-center term,

$$\epsilon_{1,1}^{1s\sigma,1s\sigma} = 2\left\langle \psi_1^{1s\sigma}(R_B,\mathbf{r}_1)\left| -\frac{1}{r_{1C}} \right| 1s(\mathbf{r}_1)\right\rangle. \tag{19}$$

The third-order energy is given by

$$\epsilon_3 = \epsilon_3^{1^1S} + 2Z_B^3\epsilon_3^{1s\sigma}(R_B) + 2Z_C^3\epsilon_3^{1s\sigma}(R_C) + Z_B\epsilon_{2,1}^{1^1S,1s\sigma}(R_B) + Z_C\epsilon_{2,1}^{1^1S,1s\sigma}(R_C) + Z_B^2\epsilon_{1,2}^{1^1S,1s\sigma}(R_B) + Z_C^2\epsilon_{1,2}^{1^1S,1s\sigma}(R_C) + 2Z_B^2Z_C\epsilon_{2,1}^{1s\sigma,1s\sigma}(R_B,R_C,\Theta) + 2Z_BZ_C^2\epsilon_{1,2}^{1s\sigma,1s\sigma}(R_B,R_C,\Theta) + Z_BZ_C\epsilon_{1,1,1}^{1^1S,1s\sigma,1s\sigma}(R_B,R_C,\Theta). \tag{20}$$

All of the singly-subscripted coefficients above are either known exactly[13] or are known to high precision from variational perturbation calculations.[11] The remaining multiperturbation coefficients can be computed, via Eqs. (11), from the appropriate components of the first-order wave function.

The total energy through nth order, in atomic units, is given by

$$E_n(R_B,R_C,\Theta) = Z_A^2\sum_{p=0}^{n} Z_A^{-p}\epsilon_p + \frac{Z_AZ_B}{R_B} + \frac{Z_AZ_C}{R_C} + \frac{Z_BZ_C}{R_{BC}}. \tag{21}$$

The total wave function, truncated through first order, can also be used to obtain a variational bound on the energy

$$E_v = Z_A^2\epsilon_0 + Z_A\epsilon_1 + \frac{\epsilon_2 + \epsilon_3/Z_A}{1 + Z_A^{-2}\langle\psi_1|\psi_1\rangle} + \frac{Z_AZ_B}{R_B} + \frac{Z_AZ_C}{R_C} + \frac{Z_BZ_C}{R_{BC}}. \tag{22}$$

Results for both the third-order perturbation sums and this variational energy for H_3^+-like systems are presented in the tables, where they are compared with accurate, variationally obtained energies.

IV. METHOD

The first-order wave functions required by the method have been obtained variationally. To simplify the calculation of the multicenter integrals that appear in the energy expansion coefficients, we have used single-center basis sets for all wave functions. Hence,

$$\psi_1^{1^1S}(\mathbf{r}_1,\mathbf{r}_2) = (1+P_{12})\sum_{nml} c_{nml}r_1^n r_2^m P_l(\cos\theta_{12}) \times \exp[-\beta_l(r_1+r_2)], \tag{23}$$

$$\psi_1^{1s\sigma}(R,\mathbf{r}_i) = \sum_{nl} c_{nl}r_i^n P_l(\cos\theta_i)\exp(-\beta_l' r_i). \tag{24}$$

For the ''atomic'' wave function, Eq. (23), all terms with $l \leq 16$ and $n+m+2l \leq 20$ were included for a total of 501 terms. For the ''molecular'' wave function, Eq. (24), all 221 terms with $l \leq 16$ and $l+n \leq 20$ were utilized. For both wave functions, the nonlinear parameters, β_l, of each partial wave were separately optimized. Once obtained, the optimized ''atomic'' wave function is stored. The nonlinear parameters for the ''molecular'' wave function, however, must be optimized for each value of the internuclear distance, R. For the sake of efficiency, these parameters were obtained at intervals of 0.10 bohr (and at smaller intervals near the equilibrium distances). These were then used to interpolate for the parameters at other values of R. Since the calculation of these one-electron, ''molecular'' wave functions is extremely rapid, it costs little in efficiency to simply recalculate them as needed. Hence, none of these ''molecular'' wave functions were stored and only the interpolation table for the nonlinear parameters was saved.

With these wave functions in hand, it only remains to calculate the energy expansion coefficients for each particular choice of R_B, R_C, and Θ. These can be calculated very efficiently; for each such point, the entire calculation of the energy through third order for all values of Z of interest consumes about 20 s of cpu time on an IBM 9021 vector processor with 2 cpu's. Hence, to calculate all the data actually presented in the tables to follow requires less than 20 min of cpu time. Even greater efficiency is possible in cal-

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TABLE I. Some perturbation energy coefficients (in a.u.); a comparison of the present results with exact values.[a]

R (bohr)	$-\epsilon_2^{1s\sigma}$ [b]	$-\epsilon_3^{1s\sigma}$ [c]	$\epsilon_{1,1}^{1^1S,1s\sigma}$ [d]	$\epsilon_{1,1}^{1s\sigma,1s\sigma}$ [e]
0.40	0.386 56	−0.022 30	0.529 45	−0.583 15
	0.386 57	−0.022 29	0.529 60	−0.583 17
0.60	0.312 05	−0.017 50	0.448 98	−0.339 32
	0.312 08	−0.017 44	0.449 10	−0.339 37
0.80	0.249 18	−0.005 93	0.367 98	−0.160 36
	0.249 21	−0.005 86	0.368 11	−0.160 37
1.00	0.199 27	0.005 97	0.293 88	−0.044 58
	0.199 31	0.005 99	0.294 00	−0.044 60
1.20	0.160 29	0.015 08	0.229 98	0.022 67
	0.160 33	0.015 17	0.230 08	0.022 68
2.00	0.070 19	0.023 14	0.075 03	0.068 73
	0.070 25	0.023 25	0.075 09	0.068 74
3.00	0.025 67	0.011 02	0.015 36	0.032 972
	0.025 69	0.011 07	0.015 39	0.032 974
4.00	0.009 769	0.003 59	0.002 81	0.013 910
	0.009 774	0.003 61	0.002 82	0.013 911

[a]Each first entry below corresponds to the present results.
[b]The second entry in this column corresponds to the results of Ref. 12.
[c]The second entry in this column corresponds to the results of Ref. 13.
[d]The second entry in this column corresponds to the results of Ref. 4(b).
[e]These results are for $\Theta=180°$, the second entry in this column corresponding to the results of Ref. 14.

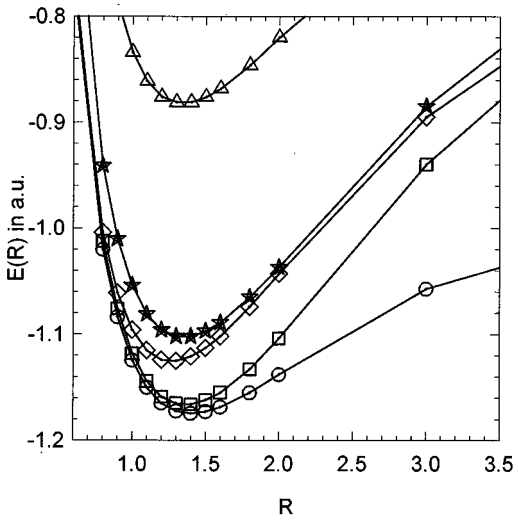

FIG. 1. Energy for H_2; (△) E_1; (◇) E_2; (□) E_3; (⋆) E_v; (○) variational results of Ref. 15.

culating the potential energy surfaces presented in the figures. For each value of R_B, R_C, the energies for all Θ of interest are calculated together. Since all coefficients that do not depend on Θ are not recalculated, less than 10 s of cpu time is required for each point. Additional savings in computational time are possible whenever $R_B=R_C$ so that many of the multiperturbation coefficients are identical.

In Table I we compare exact values[12,13] of $\epsilon_2^{1s\sigma}$ and $\epsilon_3^{1s\sigma}$ with those obtained with our approximate $\psi_1^{1s\sigma}$ and find that the approximate coefficients are accurate to at least four decimal places over the entire range of internuclear distances considered here. The simple wave function utilized here for $\psi_1^{1^1S}$ yields values for $\epsilon_2^{1^1S}$ and $\epsilon_3^{1^1S}$ which agree with accurate values of these coefficients to three decimal places. In Table I we also compare calculated and exact values[4] of $\epsilon_{1,1}^{1^1S,1s\sigma}$. Here the results obtained with the ''atomic'' first-order wave function are accurate to four decimal places, except for $R\leqslant 1$, where they are in error by roughly one unit in the fourth decimal place. (These are obtained with greater accuracy if calculated with $\psi_1^{1s\sigma}$.) Comparing exact values of $\epsilon_{1,1}^{1s\sigma,1s\sigma}$ (Ref. 14) with those calculated with the approximate first-order ''molecular'' wave function shows that the latter agree with the exact values to four or five decimal places. Not surprisingly, the approximate one-electron ''molecular'' first-order wave functions are more accurate than the two-electron ''atomic'' wave functions, but between them, they appear capable of calculating the ''mixed'' perturbation energy coefficients to roughly four decimal places for the range of R considered here. Note that, in calculating the total energies, only exact values of these coefficients have been used where they are available. Hence, the total energies presented in the tables cannot be expected to agree with accurate variational energies to more than four decimal places. Conversely, if the present calculations agree with accurate variational energies by less than about four decimal places, the discrepancy can be attributed to the truncation of the perturbation series.

V. RESULTS AND DISCUSSION

Although the main focus of this work is the calculation of polyatomic molecular energies, a brief examination of results for diatomic molecules will illustrate the behavior of the multiperturbation series in the present method.

A. Diatomic molecules: H_2

A comparison of the present perturbation results with accurate variational calculations[15] for the ground state of the H_2 molecule is presented in Fig. 1. In this figure, the convergence of the perturbation results can be gauged by examining the behavior of successive truncated perturbation sums, the E_n of Eq. (21), for the total energy of the molecule. These results indicate that the variational energy, E_v, obtained with the first-order wave function is consistently less accurate than the corresponding truncated third-order energy sum, E_3, obtained with the same wave function. This is not unexpected, as variational expressions based on perturbation wave functions such as that of Eq. (22) seem to consistently yield poorer results than the corresponding truncated perturbation series. In fact, in this instance at least, E_v is less accurate than E_2. It is also interesting to note that E_2 is quite similar to the Hartree–Fock result[16] for this molecule.

The present calculations have been carried out in sufficient detail to verify that all the E_n and E_v have a minimum in the potential energy close to the equilibrium internuclear distance for this molecule. E_3 yields the best result at $R=1.36$ bohr, within 0.04 bohr of the correct value of 1.40 bohr. Figure 2 displays differences between the ''exact'' variational results and the perturbation results,

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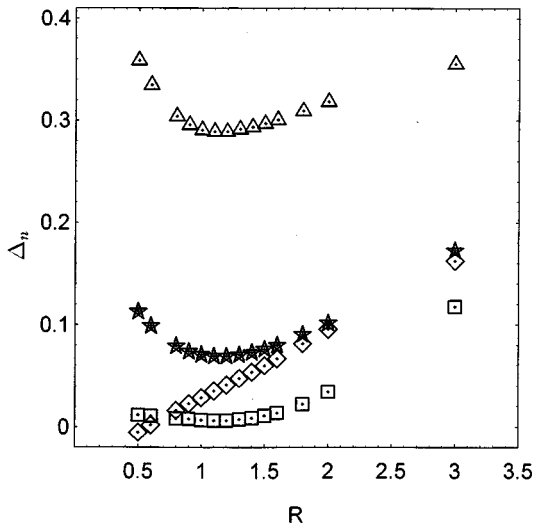

FIG. 2. Truncation error, Δ_n, for H_2; (△) Δ_1; (◇) Δ_2; (□) Δ_3; (⋆) E_v.

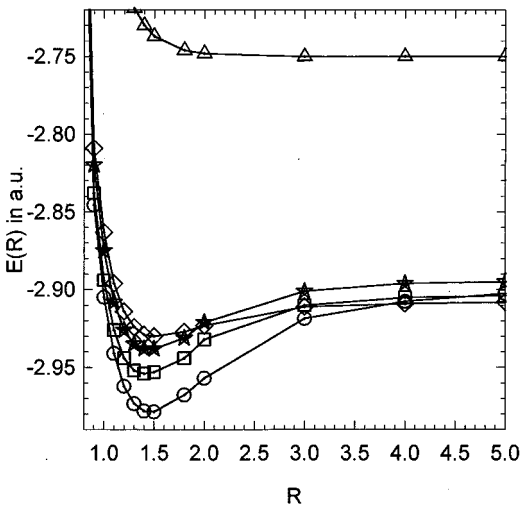

FIG. 3. Energy for HeH^+; (△) E_1; (◇) E_2; (□) E_3; (⋆) E_v; (○) variational results of Ref. 17.

$$\Delta_n = E_n - E_{\text{exact}},$$

showing that the perturbation results are most accurate in the vicinity of the energy minimum. For example, the smallest error in E_3 occurs at $R=1.2$ bohr where it is 0.006 a.u., or 0.5%. For larger R, all the perturbation results become increasingly less accurate, so that by $R=3$ the error is approximately 0.1 a.u. By $R=5$ the error for E_2, E_3, and E_v has grown to ≈ 0.25 a.u., a relative error of just over 25%. The present method fails to give accurate results for large R for this molecule since the zero-order wave function tends to an incorrect separated-atom limit ($H^- + H^+$). H_2 is, of course, a particularly difficult case for the Z^{-1} expansion. Nevertheless, the convergence of the perturbation expansion for this particular molecule is quite satisfactory. For this system, ϵ_3 is negative for the entire range of R presented in the table except for the smallest R and it provides a considerable improvement over the second-order results of Chisholm and Lodge,[4] reducing the error in the energy by almost an order of magnitude. In fact, the present results show that the relative error for E_3 remains under 1% for $1 \lesssim R \lesssim 2$ bohr.

In general, use of similar zero-order wave functions in homonuclear molecules should produce perturbation series which converge most rapidly for intermediate values of the internuclear distance, but become suspect for larger values of R.

B. Diatomic molecules: HeH^+

Figures 3 and 4 present results for HeH^+ in a form similar to those for H_2. For this molecular ion, all perturbation parameters are equal to $\frac{1}{2}$ and a more rapid convergence of the perturbation series can be expected. Moreover, unlike the case of H_2, the zero-order wave function does represent the separated-atom limit correctly. Thus, for large R, the perturbation results are very well converged except for E_1, where the discrepancy is primarily due to the absence of $\epsilon_2^{1^1S}$. For this system, we find that E_2 and E_3 give slightly better results at both larger and smaller internuclear distances rather than at the equilibrium distance. Indeed, E_3 does not yield quite as good an equilibrium distance as either E_2 or E_v; $R=1.41$ as compared to $R=1.50$ and 1.43, respectively. All however lie within 0.05 bohr of the correct value of $R=1.463$ (Ref. 17). In contrast to the other systems studied here, E_v is consistently better than both E_2 and the Hartree–Fock energy[18] for $R \lesssim 2$. Again, as in the case of H_2, E_2 and the Hartree–Fock energy are quite similar for $R \lesssim 2$, beyond which point E_2 is a significant improvement over E_v. Since the perturbation series for this molecule converges more rapidly, the improvement that E_3 provides over E_2 is not as large here as in the case of H_2. Nevertheless, E_3 generally reduces the error relative to accurate variational results[17] to less than half what it was for E_2. Over the entire range of R, the relative error in E_3 is less than 1% for this molecule. Indeed, it is less than 0.5% for $1.0 \gtrsim R \gtrsim 2.5$.

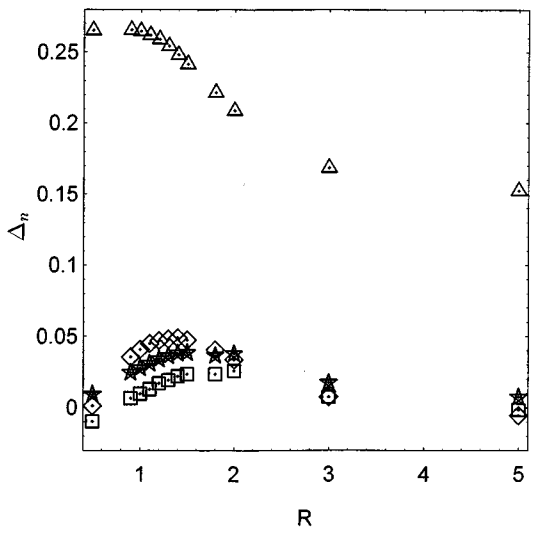

FIG. 4. Truncation error, Δ_n, for HeH^+; (△) Δ_1; (◇) Δ_2; (□) Δ_3; (⋆) E_v.

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TABLE II. Total energies (in a.u.) for the H_3^+ molecule; the first-order variational energy, E_v, and truncated energy sums, E_n, compared with variational energies.

			D_{3h} Symmetry		
R (bohr)	E_v	E_1	E_2	E_3	E(variational)[a]
1.137	−0.913	−0.481	−1.265	−1.230	−1.233 78
1.250	−1.015	−0.584	−1.282	−1.304	−1.286 40
1.277	−1.033	−0.603	−1.283	−1.317	−1.295 48
1.414	−1.105	−0.678	−1.280	−1.365	−1.327 44
1.549	−1.145	−0.724	−1.265	−1.387	−1.341 24
1.644	−1.159	−0.743	−1.249	−1.391	−1.343 79
1.650	−1.160	−0.744	−1.248	−1.391	−1.343 83
1.656	−1.161	−0.745	−1.247	−1.391	−1.343 78
1.819	−1.166	−0.762	−1.215	−1.381	−1.338 33
1.900	−1.163	−0.765	−1.197	−1.370	−1.331 39[b]
2.050	−1.150	−0.764	−1.163	−1.343	−1.319 13
2.094	−1.145	−0.763	−1.153	−1.334	−1.314 56
2.200	−1.130	−0.758	−1.128	−1.310	−1.301 51[b]
2.235	−1.125	−0.756	−1.120	−1.302	−1.298 63
2.750	−1.032	−0.716	−1.009	−1.166	−1.234 12[b]
3.052	−0.975	−0.691	−0.954	−1.088	−1.198 43[b]
3.350	−0.923	−0.667	−0.907	−1.018	−1.166 32[b]
4.500	−0.776	−0.597	−0.787	−0.831	−1.076 51[b]
5.500	−0.706	−0.557	−0.730	−0.746	−1.036 26[b]
7.000	−0.649	−0.518	−0.681	−0.682	−1.011 21[b]

			C_{2v} Symmetry			
R (bohr)	Θ	E_v	E_1	E_2	E_3	E(variational)[a]
1.130	124.141	−1.041	−0.857	−1.307	−1.131	−1.238 38
1.257	117.047	−1.117	−0.918	−1.313	−1.205	−1.278 81
1.431	114.447	−1.174	−0.969	−1.298	−1.254	−1.301 07
1.435	109.417	−1.174	−0.957	−1.305	−1.262	−1.305 22
1.438	132.515	−1.180	−1.004	−1.270	−1.239	−1.289 43
1.452	99.513	−1.175	−0.931	−1.315	−1.282	−1.314 26
1.462	95.863	−1.176	−0.920	−1.317	−1.291	−1.317 79
1.507	82.960	−1.179	−0.875	−1.316	−1.328	−1.330 28
1.509	157.418	−1.195	−1.037	−1.235	−1.237	−1.281 33
1.537	76.835	−1.179	−0.847	−1.309	−1.348	−1.335 63
1.571	70.958	−1.176	−0.817	−1.295	−1.365	−1.339 92
1.609	65.344	−1.170	−0.783	−1.275	−1.380	−1.342 76
1.619	103.498	−1.194	−0.963	−1.283	−1.285	−1.309 96
1.695	54.929	−1.165	−0.764	−1.262	−1.385	−1.342 62
1.743	50.129	−1.166	−0.781	−1.273	−1.375	−1.338 81
1.756	20.043	−0.353	0.310	−0.320	−0.784	−0.889 35
1.756	99.957	−1.193	−0.955	−1.261	−1.287	−1.304 81
1.794	45.594	−1.164	−0.795	−1.281	−1.361	−1.331 83
1.848	41.316	−1.156	−0.805	−1.284	−1.341	−1.321 02
1.894	23.069	−0.872	−0.606	−1.150	−1.029	−1.086 63
1.962	33.488	−1.122	−0.807	−1.274	−1.283	−1.284 03
1.995	31.510	−1.107	−0.802	−1.266	−1.263	−1.269 23
2.085	26.551	−1.050	−0.771	−1.230	−1.193	−1.215 80
2.154	68.199	−1.175	−0.828	−1.229	−1.343	−1.316 90[b]
2.277	29.448	−1.130	−0.840	−1.244	−1.265	−1.267 52
2.419	31.275	−1.153	−0.859	−1.234	−1.285	−1.280 59
3.092	75.964	−1.138	−0.870	−1.175	−1.243	−1.245 92[b]
4.067	79.588	−1.114	−0.877	−1.143	−1.195	−1.201 25[b]
5.054	81.637	−1.104	−0.878	−1.129	−1.177	−1.182 25[b]
6.044	83.063	−1.102	−0.878	−1.123	−1.170	−1.176 28[b]
8.031	84.928	−1.102	−0.880	−1.122	−1.167	−1.174 04[b]
10.025	85.939	−1.101	−0.880	−1.121	−1.166	−1.173 45[b]

[a]Unless otherwise noted, these are all from Frye *et al.*, Ref. 19.
[b]Talbi and Saxon, Ref. 20.

C. Triatomic molecules: H_3^+

As in the case of H_2, this molecule presents a severe test for the method. In addition to slow convergence, the calculated ground state energies also have the same difficulties at the separated-atom limit noted for H_2. Table II presents results for H_3^+ in D_{3h} (equilateral triangle) and C_{2v} (isosceles triangle) symmetry. In addition, Figs. 5, 6, and 7 present potential energy surfaces based on E_1, E_2, and E_3 for C_{2v}

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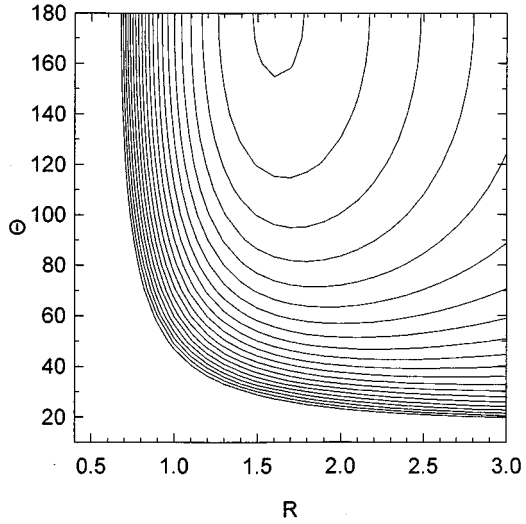

FIG. 5. E_1 potential energy surface for H_3^+; contours are 0.05 a.u. apart starting at -1.19 a.u.

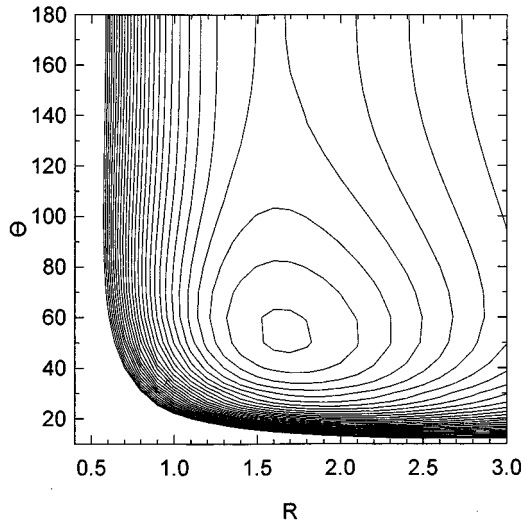

FIG. 7. E_3 potential energy surface for H_3^+; contours are 0.05 a.u. apart starting at -1.39 a.u.

symmetry. In Fig. 5, we see that E_1 does not reproduce the correct equilibrium separation for D_{3h} symmetry. Surprisingly, however, it does yield an equilibrium distance of $R=1.62$ at the minimum of its potential energy surface, close to the correct value of $R=1.65$, but this occurs for a linear geometry. Note that the *only* dependence on Θ at this order is through the nuclear potential, $Z_B Z_C / R_{BC}$. Adding the second-order energy introduces the first Θ-dependent contribution to the electronic energy. The overall second-order coefficient is everywhere negative and becomes more so for small R and Θ. This places the minimum of the potential in Fig. 6 at $R=1.20$, $\Theta=90°$, shifting the minimum in the right direction but by too much in R and not enough in Θ. The third-order energy coefficient itself has a minimum very close to the correct equilibrium distance for the molecule, but at $\Theta=0°$. As a consequence, this coefficient produces a minimum in the potential energy very close to the correct equilibrium separation but slightly too low in Θ. The potential energy surface of Fig. 7 shows a minimum energy at $R=1.66$ and $\Theta=54°$. In contrast, the potential produced by E_v and displayed in Fig. 8 shows a long trough with a shallow secondary minimum at its head near $\Theta=90°$ and the minimum at its base at $\Theta=180°$. Of course the energy for this minimum lies well above those of E_2 and E_3.

A number of variational calculations have been carried out to an accuracy of a few thousandths a.u. or better for this molecule. Notable among these are the calculations of Frye *et al.*,[19] who obtain very accurate results over a range of internuclear separations and geometries. Total energies for larger internuclear distances can be found in Talbi and Saxon.[20] The accuracy of these calculations permit an unambiguous assessment of the convergence of the perturbation results. A comparison of these results for D_{3h} and C_{2v} sym-

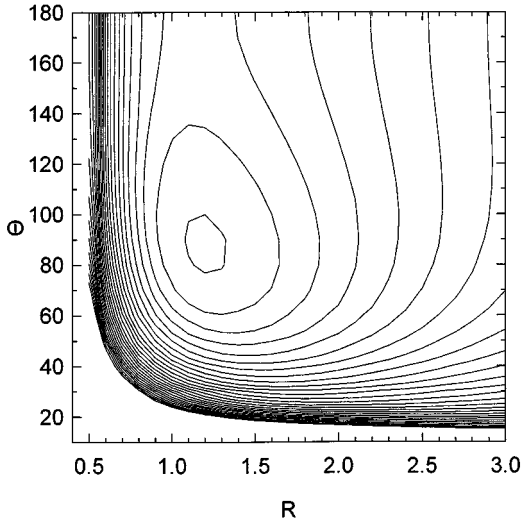

FIG. 6. E_2 potential energy surface for H_3^+; contours are 0.05 a.u. apart starting at -1.21 a.u.

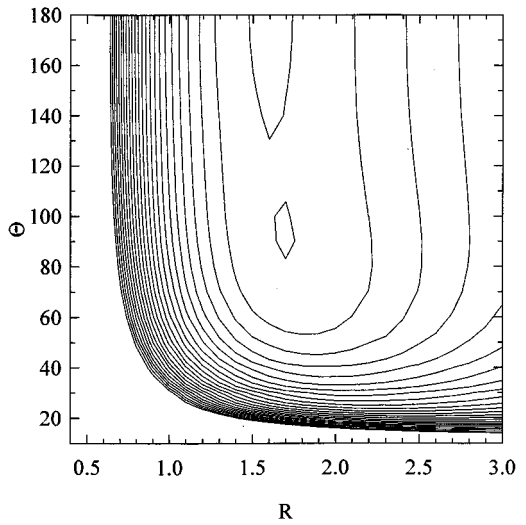

FIG. 8. E_v potential energy surface for H_3^+; contours are 0.05 a.u. apart starting at -1.19 a.u.

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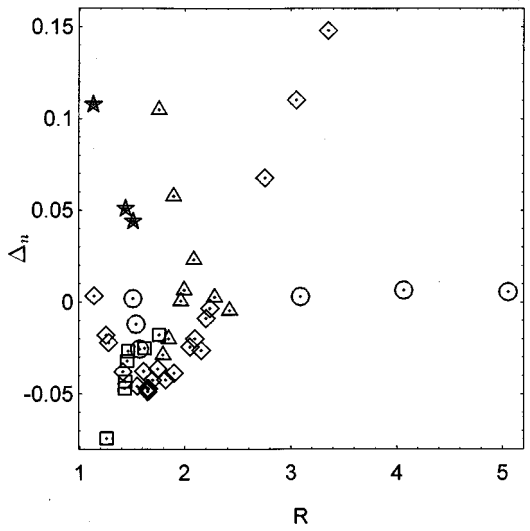

FIG. 9. Truncation error, Δ_3, for H_3^+; (△) $\Theta<50°$; (◇) $50°<\Theta<70°$; (○) $70°<\Theta<90°$; (□) $90°<\Theta<120°$; (⋆)$\Theta>120°$.

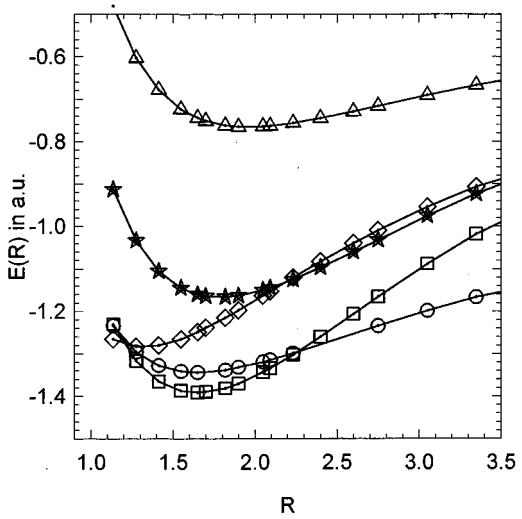

FIG. 10. Energy for equilateral H_3^+; (△) E_1; (◇) E_2; (□) E_3; (⋆) E_v; (○) variational results, Ref. 17.

metries is presented in Table II. Figure 9 displays the differences between the variational values and E_3, grouped according to the value of Θ. In the vicinity of the equilibrium distance, most points fall in the range of ± 0.05 a.u., a relative error of about 3.5%. Exceptions to this occur for those points with both the largest and the smallest values of Θ; i.e., all those with $\Theta>120°$ and two points belonging to the group with $\Theta<50°$ that actually have the smallest values of $\Theta(\approx 20°)$. These all have relative errors ranging from 5% to 10%. At larger internuclear distances, points with $\Theta=60°$ show an error which increases with R, while points which correspond to $\Theta\approx 90°$ have an error which remains fairly constant at about 0.006 a.u. It is clear that much of this behavior is determined by the initial charge distribution imposed by the zero-order function. Thus, those points with $R>3$ and $\Theta\approx 90°$, all of which have geometries with one internuclear distance held close to the equilibrium separation for H_2,[20] have errors which are quite close to that of the H_2 molecule at equilibrium, the perturbation coefficients involving large internuclear separations contributing little to the total energy. Conversely, those points at large R corresponding to an equilateral geometry all have errors which increase with R in a manner similar to the results for H_2 at large R.

D. Equilateral H_3^+

For the equilateral geometry, a comparison to H_2 is useful throughout the entire range of R. Figures 10 and 11 present the results for equilateral H_3^+ in a manner similar to Figs. 1 and 2 for H_2. Comparison of Figs. 2 and 11 indicates that, in this case, the errors for E_n in H_3^+ behave very much like the corresponding errors in H_2, although these are, in general, considerably smaller for H_2. For example, for R in the range $1.2<R<1.8$, errors in H_3^+ are roughly 2 to 5 times larger than those found for H_2 at similar internuclear distances. Ultimately, and again as in the case of H_2, as R increases these results converge more slowly and to the wrong limiting value. Thus, the relative error in E_3 increases steadily for increasing R, reaching 5% in the vicinity of $R\approx 2.7$ and 10% by $R\approx 3$. However, for $1<R<2.5$, the relative error is always less than 3.5%. Both E_3 and E_v (but not E_2) predict a minimum in the potential energy for this symmetry at the correct internuclear distance to within ± 0.01 bohr. Surprisingly, E_3 is more negative than the "exact" variational values for $1.25<R<2.5$, reaching its greatest discrepancy in the vicinity of the equilibrium position. However, as in the case of H_2, these results show a satisfactory convergence and a significant improvement in the total energy over the second-order results.

For nonsymmetric geometries of this molecule, comparison to the results of Ref. 19 shows that the truncation error is generally about 0.02–0.05 a.u. for the internuclear distances considered there, with the range from largest to smallest being from 0.006 to 0.09 a.u.

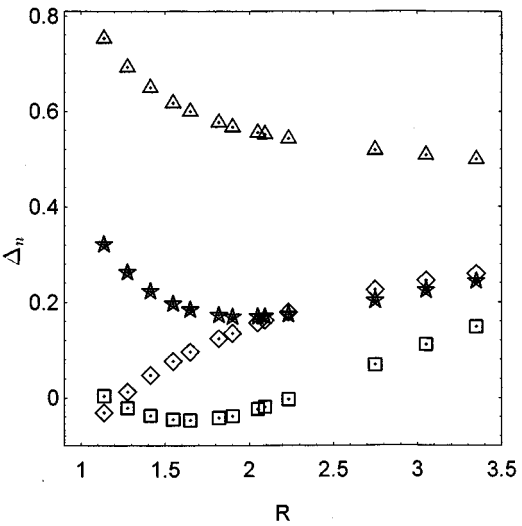

FIG. 11. Truncation error, Δ_n, for equilateral H_3^+; (△) Δ_1; (◇) Δ_2; (□) Δ_3; (⋆) E_v.

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TABLE III. Total energies (in a.u.) for the linear, symmetric HeH_2^{++} molecule; the first-order variational energy, E_v, and truncated energy sums, E_n, compared with the variational results.

R (bohr)	E_v	E_1	E_2	E_3	E(variational)[a]
1.00	−2.188	−2.030	−2.181	−2.197	−2.155 91
1.50	−2.552	−2.390	−2.554	−2.564	−2.527 73
2.00	−2.653	−2.497	−2.660	−2.664	−2.625 87
2.50	−2.700	−2.550	−2.710	−2.710	−2.663 36
3.00	−2.730	−2.583	−2.742	−2.739	−2.683 70
3.50	−2.753	−2.607	−2.765	−2.762	−2.698 66
4.00	−2.770	−2.625	−2.783	−2.779	−2.711 56
4.50	−2.784	−2.639	−2.797	−2.792	−2.722 94
5.00	−2.795	−2.650	−2.808	−2.803	−2.732 74

[a]Zetik and Poshusta, Ref. 21.

E. Triatomic molecules: HeH_2^{+2}

Comprehensive variational calculations for this unstable system over a range of internuclear distances can be found in Zetik and Poshusta[21] who examined the potential energy surface for a linear geometry. These results are compared with the present calculations in Table III and Fig. 12 for the linear, symmetric molecule. This comparison shows that E_2, E_3, and E_v all lie below this variational calculation by roughly 0.05 a.u. Since E_v is itself an upper bound to the exact energy, it is clear that all of these results represent an improvement over the variational result. Note that both E_2 and E_3 lie lower in energy than E_v for $R \geqslant 1$, with E_2 being the more negative for $R > 2.5$. The absolute accuracy of these results is difficult to judge in the absence of more accurate variational calculations. Recalling the comparable behavior of the perturbation series for H_3^+ and H_2 noted earlier, a corresponding similarity between the HeH_2^{++} and HeH^+ series might be expected. Indeed, the E_n of Table III do suggest a rapid convergence of the perturbation series for HeH_2^{++}. In particular, ϵ_3 for this system is virtually identical to ϵ_3 for HeH^+ once R exceeds about 2 bohr, indicating that contributions from multiperturbation coefficients with two ''molecular'' perturbations, as appear in polyatomic systems, are quite small for large R. In fact, the only significant contribution to ϵ_3 in this range of R is from $\epsilon_3^{1^1S}$. In this context, it should be remembered that internuclear distances are scaled by the nuclear charge, Z_A, so that these energy coefficients are actually calculated with values of R that are twice their nominal value in bohr.

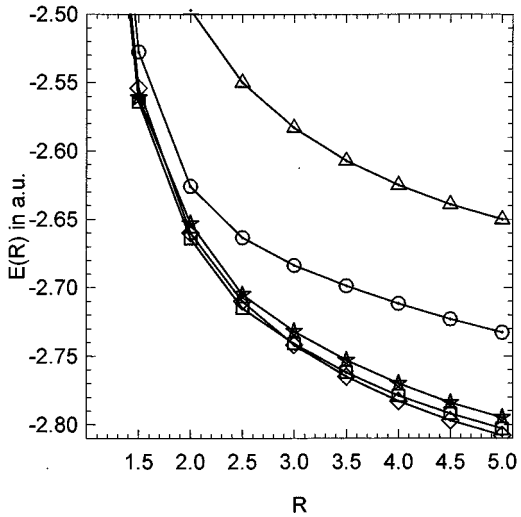

FIG. 12. Energy for linear, symmetric HeH_2^{++}; (△) E_1; (◇) E_2; (□) E_3; (⋆) E_v; (○) variational results of Ref. 21.

Similar improvements in convergence can be expected for molecules containing heavier atoms than those appearing in these two-electron systems. This should be particularly true for heteronuclear molecules, especially those with a single heavy ion. For homonuclear molecules, where the multiperturbation parameter $\lambda_M = 1$, the relative error (in charge-scaled atomic units) can actually increase with Z along a particular isoelectronic sequence, while the absolute error remains roughly constant. In *nonscaled* atomic units, the absolute error increases as $Z_A^2 \epsilon_{n+1}^M$. This error is easily corrected, however, by simply adding the ''missing'' portion of the electronic energy of the appropriate states of the one-electron diatomic molecule.

VI. SUMMARY

In Z-dependent perturbation theory, the lowest-order wave functions for a polyatomic molecule are not only independent of the nuclear charges, but are also independent of the total number of nuclear centers and electrons in the molecule. The complexity of the problem is then determined by the highest order of the calculation. With the present choice of H_0, the first-order wave function for any polyatomic molecule is described completely in terms of two-electron, one-center (atomic) and one-electron, two-center (molecular) first-order wave functions. These are separately obtained from calculations on He-like and H_2^+-like systems. At nth-order the wave function for a polyatomic molecule decouples into a sum over the nth-order wave functions of all p-electron, q-center subsystems ($p+q=n+2$) that are contained within the molecule of interest.

We have illustrated the application of this method with some results, complete through third order in the energy, for H_3^+-like molecules. In applying this method, we have chosen to describe the system by a zero-order wave function that minimizes the complexity of the calculations. The perturbation series calculated through third order essentially yield the

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correct equilibrium internuclear distance and geometry, even in the case of H_3^+. For this molecule, the perturbation series is best converged in the vicinity of the equilibrium distance. For larger R, the truncation error remains small if one of the internuclear distances is held near the equilibrium distance. However, if all internuclear distances are increased, the truncation error increases as a consequence of the incorrect separated-atom limit of the zero-order wave function. In the case of HeH_2^{++}, the convergence of the perturbation series is significantly improved, particularly in the vicinity of the separated-atom limit.

The present calculations can be improved without significant complication of the method by introducing a screened nuclear charge for the unperturbed Hamiltonian[22] or by repositioning the unperturbed, single-center Hamiltonian away from the physical charges.[3] Calculations incorporating these improvements and extending this initial study to higher-order are currently underway.

For all diatomic and polyatomic systems examined here, the perturbation energy summed through third order generally yields results comparable in accuracy to variational calculations of moderate size and complexity. Given the simplicity and efficiency of the method, these results for simple systems are very encouraging. Since, through a given order in the perturbation, the computations are of a fixed degree of complexity regardless of the size of the molecule, application to larger systems with higher Z seems promising.

APPENDIX: THREE-ELECTRON MOLECULES

The zero-order wave function for the three-electron, three-center molecule is degenerate, while a more complex, permutational symmetry not present in the ground state of the corresponding two-electron molecule also appears here. Expressions for the first-order wave function and second-order energy of this system are obtained here to illustrate how these affect the multiperturbation expansion. The doubly-degenerate zero-order wave function for this system is

$$\psi_0 = c_s \psi_0^s + c_p \psi_0^p ,$$

where

$$\psi_0^l = 2^{-(1/2)}(1-P_{13})1s(\mathbf{r}_1)1s(\mathbf{r}_2)2l(\mathbf{r}_3)$$

for $l=s$ or p. The coefficients, c_l, are the eigenvectors of the perturbation matrix formed with these degenerate wave functions. The eigenvalues are just the first-order energies,

$$\epsilon_1 = \frac{\epsilon_1^s + \epsilon_1^p}{2} \pm \frac{\epsilon_1^s - \epsilon_1^p}{2} \sqrt{1 - \left(\frac{2V}{\epsilon_1^s - \epsilon_1^p} \right)^2} ,$$

where

$$\epsilon_1^l = \epsilon_1^{a,l} + Z_B \epsilon_1^{m,l}(R_B) + Z_C \epsilon_1^{m,l}(R_C),$$

with

$$\epsilon_1^{a,l} = \epsilon_1^{1^1S} + \frac{1}{2}\,\epsilon_1^{2^1L} + \frac{3}{2}\,\epsilon_1^{2^3L} ,$$

and

$$\epsilon_1^{m,l}(R_\alpha) = 2\epsilon_1^{1s\sigma}(R_\alpha) + \epsilon_1^{2l\sigma}(R_\alpha).$$

Here the $\epsilon_1^{2^{1,3}L}$ are the first-order corrections to the singlet and triplet $2S$ and $2P$ states of the two-electron atom, while

$$\epsilon_1^{2l\sigma}(R_\alpha) = -\left\langle 2l(\mathbf{r}) \left| \frac{1}{r_\alpha} \right| 2l(\mathbf{r}) \right\rangle ,$$

$$\epsilon_1^{2s\sigma}(R) = \frac{1}{4R} - \frac{1}{4R}\,(1 + \tfrac{3}{4}R + \tfrac{1}{4}R^2 + \tfrac{1}{8}R^3)e^{-R},$$

$$\epsilon_1^{2p\sigma}(R) = \frac{3}{R^3} + \frac{1}{4R} - \left[\frac{3}{R^3}\,(1+R) + \frac{1}{4R}\,(7 + \tfrac{11}{4}R + \tfrac{3}{4}R^2 + \tfrac{1}{8}R^3) \right] e^{-R}.$$

The off-diagonal matrix element, $V = Z_B v_{2s,2p}(R_B) + Z_C v_{2s,2p}(R_C)$, with

$$v_{2s,2p}(R) = -\left\langle 2s(\mathbf{r}) \left| \frac{1}{r_\alpha} \right| 2p(\mathbf{r}) \right\rangle = -\frac{3}{4R^2} + \left[\frac{3}{4R^2}\,(1+R) + \tfrac{1}{8}(3 + R + \tfrac{1}{4}R^2) \right] e^{-R}.$$

The complete first-order wave function is then given by

$$\psi_1 = c_s \psi_1^s + c_p \psi_1^p + \gamma \psi_0' ,$$

where

$$\psi_0' = -c_p \psi_0^s + c_s \psi_0^p$$

appears as an admixture of the other degenerate, zero-order wave function (without, however, contributing to the second-order energy). Also,

$$\psi_1^l = \psi_1^{a,l} + Z_B \psi_1^{m,l}(R_B) + Z_C \psi_1^{m,l}(R_C),$$

where the $\psi_1^{a,l}$ are the first-order wave functions for the ground and lowest ^2P-state of three-electron atoms. These can be expressed completely in terms of the first-order wave functions of two-electron atoms,[23]

$$\psi_1^{a,l} = 2^{-(1/2)}(1-P_{13})\{\psi_1^{1^1S}(\mathbf{r}_1,\mathbf{r}_2)2l(\mathbf{r}_3) + 2^{-(1/2)} \times [\psi_1^{2^1L}(\mathbf{r}_2,\mathbf{r}_3)1s(\mathbf{r}_1) + \psi_1^{2^3L}(\mathbf{r}_2,\mathbf{r}_3)1s(\mathbf{r}_1) + \psi_1^{2^3L}(\mathbf{r}_1,\mathbf{r}_3)1s(\mathbf{r}_2)]\}.$$

The $\psi_1^{m,l}(R_\alpha)$ can be constructed entirely from first-order, H_2^+-like wave functions,

$$\psi_1^{m,l}(R_\alpha) = 2^{-(1/2)}(1-P_{13})[\psi_1^{1s\sigma}(R_\alpha,\mathbf{r}_1)1s(\mathbf{r}_2)2l(\mathbf{r}_3) + \psi_1^{1s\sigma}(R_\alpha,\mathbf{r}_2)1s(\mathbf{r}_1)2l(\mathbf{r}_3) + \psi_1^{2l\sigma}(R_\alpha,\mathbf{r}_3)1s(\mathbf{r}_1)1s(\mathbf{r}_2)],$$

where $\psi_1^{2l\sigma}$ are solutions to the degenerate, first-order, perturbation differential equation for the $2l$ zero-order wave function,[10] e.g.,

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$$G_0\psi_1^{2s\sigma}(R_\alpha,\mathbf{r})-\left(\frac{1}{r_\alpha}+\epsilon_1^{2s\sigma}\right)2s(\mathbf{r})-v_{2s,2p}(R_\alpha)2p(\mathbf{r})=0.$$

This first-order wave function then yields the second-order energy coefficient,

$$\epsilon_2=\epsilon_2^{1s^2}+c_s^2\epsilon_2^s+c_p^2\epsilon_2^p+c_sc_p\epsilon_2^{s,p},$$

where $\epsilon_2^{1s^2}$ is given by Eq. (18), the second-order energy for the ground state of an H_3^+-like molecule,

$$\epsilon_2^l=\epsilon_2^{a,l}+Z_B^2\epsilon_2^{2l\sigma}(R_B)+Z_C^2\epsilon_2^{2l\sigma}(R_C)+Z_B\epsilon_{1,1}^{a,2l\sigma}(R_B)+Z_C\epsilon_{1,1}^{a,2l\sigma}(R_C)+Z_BZ_C\epsilon_{1,1}^{2l\sigma,2l\sigma}(R_B,R_C,\Theta),$$

and

$$\epsilon_2^{s,p}=Z_B^2\epsilon_2^{2(s,p)\sigma}(R_B)+Z_C^2\epsilon_2^{2(s,p)\sigma}(R_C)+Z_B\epsilon_{1,1}^{a,2(s,p)\sigma}(R_B)+Z_C\epsilon_{1,1}^{a,2(s,p)\sigma}(R_C)+Z_BZ_C\epsilon_{1,1}^{2s\sigma,2p\sigma}(R_B,R_C,\Theta).$$

The multiperturbation coefficients appearing in this second-order energy coefficient are given by

$$\epsilon_2^{a,l}=\tfrac{1}{2}\epsilon_2^{2^1L}+\tfrac{3}{2}\epsilon_2^{2^3L}+\delta_2^l,$$

where δ_2^l is the three-electron contribution to the second-order energy of a three-electron atom,[23]

$$\epsilon_2^{2l\sigma}(R_\alpha)=-\left\langle\psi_1^{2l\sigma}(R_\alpha,\mathbf{r})\left|\frac{1}{r_\alpha}\right|2l(\mathbf{r})\right\rangle,$$

$$\epsilon_{1,1}^{a,2l\sigma}(R_\alpha)=\tfrac{1}{2}\epsilon_{1,1}^{2^1L,2l\sigma}(R_\alpha)+\tfrac{3}{2}\epsilon_{1,1}^{2^3L,2l\sigma}(R_\alpha)$$

with

$$\epsilon_{1,1}^{2^{1,3}L,2l\sigma}(R_\alpha)=-2^{1/2}\left\langle\psi_1^{2^{1,3}L}(\mathbf{r}_1,\mathbf{r}_2)\left|\frac{1}{r_{1\alpha}}+\frac{1}{r_{2\alpha}}\right|1s(\mathbf{r}_1)2l(\mathbf{r}_2)\pm2l(\mathbf{r}_1)1s(\mathbf{r}_2)\right\rangle,$$

$$\epsilon_{1,1}^{2l\sigma,2l\sigma}(R_B,R_C,\Theta)=-2\left\langle\psi_1^{2l\sigma}(R_B,\mathbf{r})\left|\frac{1}{r_C}\right|2l(\mathbf{r})\right\rangle,$$

$$\epsilon_2^{2(s,p)\sigma}(R_\alpha)=-2\left\langle\psi_1^{2s\sigma}(R_\alpha,\mathbf{r})\left|\frac{1}{r_\alpha}\right|2p(\mathbf{r})\right\rangle,$$

$$\epsilon_{1,1}^{a,2(s,p)\sigma}(R_\alpha)=\tfrac{1}{2}[\epsilon_{1,1}^{2^1S,2p\sigma}(R_\alpha)+\epsilon_{1,1}^{2^1P,2s\sigma}(R_\alpha)]+\tfrac{3}{2}[\epsilon_{1,1}^{2^3S,2p\sigma}(R_\alpha)+\epsilon_{1,1}^{2^3P,2s\sigma}(R_\alpha)],$$

and

$$\epsilon_{1,1}^{2s\sigma,2p\sigma}(R_B,R_C,\Theta)=-2\left[\left\langle\psi_1^{2s\sigma}(R_B,\mathbf{r})\left|\frac{1}{r_C}\right|2p(\mathbf{r})\right\rangle+\left\langle\psi_1^{2p\sigma}(R_B,\mathbf{r})\left|\frac{1}{r_C}\right|2s(\mathbf{r})\right\rangle\right].$$

One approach to evaluating the $\epsilon_2^{2l\sigma}$, $\epsilon_{1,1}^{2^{1,3}L,2l\sigma}$, and $\epsilon_2^{2(s,p)\sigma}$ coefficients can be found in Ref. 10.

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