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A Fifth-order Multiperturbation Derivation of the Energy Coefficients of Polyatomic Molecules

اشتقاق الرتبة الخامسة للنظرية متعددة القلقلة لمعاملات الطاقة للجزيئات متعددة الذرات

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ABSTRACT

A multiperturbation theory has been developed for molecular systems.

In the present paper we extend this theory to fifth order in the energy. The "bare-nucleus" hydrogenic function is chosen as the zero-order wave function rather than the more customary hartree-fock function. With this choice the multiperturbation wave functions are independent of the nuclear charges and of the total number of nuclear centers and electrons for the molecule, and are thus completely transferable to other systems. Making the simplest possible

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choice, 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 choice of zero-order Hamiltonian (H_0) the first-order wave function for any polyatomic molecule will consist entirely of two-electron, one-center and one-electron,two-center first-order wave functions. These are exactly transferable from calculations on He-like and H_2^+-like systems. To calculate the first-order and second-order correction for the wave function of any polyatomic molecule, we need the first-order and second-order correction for a two-electron atomic wave function, the first-order and second-order correction for a one-electron diatomic molecular wave function and some additional mixed second-order corrections. The wave functions necessary will be two-center, one-electron at most.

The second-order wave function for a polyatomic molecule contains additional contributions which cannot be obtained from the simple subsystems, but represent multiple perturbation contributions which are two-electron diatomic, and one-electron triatomic in character.

The expressions for the multiperturbation energy-expansion coefficients through fifth order are derived.

ملخـــص

النظرية متعددة القلقلة طورت للأنظمة الجزيئية.

في هذا البحث تم تطوير نظرية القلقلة للرتبة الخامسة للطاقة. الدالة الهيدروجينية تم اختيارها كرتبة الصفر لدالة الموجة بدلا من دالة هارتري فوك . بهذا الاختيار فان دوال الموجة متعددة القلقله لا تعتمد على: ١. شحنات النواه. ٢. عدد مراكز النواه. ٣. الكترونات الجزيء، وهذه الطريقة قابلة للتطبيق للأنظمة الاخرى. ولتسهيل

الطريقة تم وصف ن . الكترون، م . مركز جزيء متعدد الذرات على مركز احادي متقلقل بسبب تأثير الكترون على الكترون وتأثير الكترون على نواه. بهذا الاختيار لرتبة هاميلتون الصغري فان الرتبة الأولى لدالة الموجة لأي جزيء متعدد الذرات تتكون كليا من الكترونين، مركز واحد والكترون واحد، مركزين من الرتبة الأولى لدوال الموجة. هذه جميعا قابلة للتحويل من الحسابات على أنظمة الهيليوم (He)وعلى جزيء الهيدروجين المتأين (H_2^+)لحساب التعديل للرتبة الاولى والثانية لدالة الموجة لأي جزيء متعدد الذرات قاننا بحاجة للتعديل من الرتبة الاولى والثانية لدالة الموجه الذرية لألكترونين، وتعديل دالة الموجة لجزيء ثنائي الذرة (H_2^+) الدوال الموجية الضرورية تتكون من مركزين والكترون واحد على الأغلب.

الدالة الموجية من الرتبة الثانية متعدد الذرات تحوي اسهامات اضافية والتي لا يمكن الحصول عليها من انظمة فرعية مبسطة، ولكنها تمثل اسهامات متعددة القلقلة والتي هي جزيء ثنائي الذرة (He) وجزيء ثلاثي الذرة (H_3^{++})

لقد تم اشتقاق المعادلات للنظرية متعددة القلقلة لمعاملات الطاقة للرتبة الخامسة.

I. Introduction

In general, the nth-order wave function or energy for a polyatomic molecule decouples into a sum over all contributions from p-electron, q-center subsystems (p+q=n+2) that are contained within the molecule of interest. Hence, in nth-order, the most complex contributions to the wave function (or energy) will involve (n+1)-electron, one-center or one-electron, (n+1)-center contributions.

The fact that the multiperturbation expansion coefficents are independent of the nuclear charges and of the total electronic configuration of the system assures that results obtained for smaller subsystems are exactly transferable into larger systems of interest.(3,5)

In 1971 Chisholm and Lodge carried out a study of two-electron diatomic molecules through second order in the energy.(1,2,3) In his paper(4), Sanders has derived the energy coefficients through fourth-order correction. The two-electron polyatomic molecule has been studied through second order in the energy.(6) The third and fourth-order corrections in the energy have been calculated for homonuclear and heteronuclear diatomic and polyatomic molecules.(7)

The complete first-order wave function of any molecule can 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, single-electron diatomic (H_2^+-like) wave functions of all the orbitals in the zero-order wave function. The second-order correction to the enegry then 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 introducing either an additional electron or an additional center to the complexity of the expansion coefficients.

In this paper a fifth-order multiperturbation derivation of the energy coefficients of polyatomic molecules is presented in analogy to a similar approach for atoms.

II. Multiperturbation Theory

Consider a system described by the time-independent, non-relativistic Schrodinger equation

$$H\psi = E\psi; \qquad (1)$$

where Ψ and E are the eigenfunction and eigenvalue of the Hamiltonian H.

For a polyatomic molecule the total Hamiltonian is given by

$$H = H_o + \sum_a \lambda_a H_1^a; \qquad (2)$$

where, in charge-scaled atomic units, H_O is a sum of one-electron (hydrogenic) Homiltonians for an N-electron system:

$$H_O = \sum_{i=1}^{N} h_o(i) = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 - \frac{1}{r_i}\right) \qquad (3)$$

Here H_1^a are distinct perturbation functions and $\lambda_a^{'s}$ are the perturbation parameters. This choice of zero-order Hamiltonian allows the perturbation expansion coefficients to be independent of the nuclear charges and completely transferable from one system to another. It also reduces to a minimum the number of centers that can appear at any particular order.

The total wave function and the total energy can be represented by a series expansion(1) :

$$\psi = \sum_{l,m,n} \lambda_\alpha^l \lambda_\beta^m \lambda_\gamma^n \ldots\ldots\ldots \psi_{l,m,n,\ldots}^{\alpha,\beta,\gamma,\ldots}; \qquad (4)$$

and

$$E = \sum_{l,m,n} \lambda_\alpha^l \lambda_\beta^m \lambda_\gamma^n \ldots\ldots\ldots\ldots\ldots \epsilon_{l,m,n,\ldots}^{\alpha,\beta,\gamma,\ldots}; \qquad (5)$$

$\Psi_{n,m}^{\alpha\beta}$ and $\mathcal{E}_{n,m}^{\alpha\beta}$ being of nth order in the perturbation $\mathcal{H}_1^\alpha$ and mth order in the perturbation $\mathcal{H}_1^\beta$. By substituting Eqs (2), (4) and (5), into (1), we obtain the multiperturbation differential equations as shown in Appendix (A).

III. Energy Coefficients

The expressions for the energy coefficients can be derived in the usual manner[2] frothe multiperturbation differential equations [Appendix (A)]. The expressions for all energy coefficients complete through third order are shown in Appendix (B). The fourth and fifth-order energy coefficients are presented below :

$$\epsilon_1^\alpha = \langle \psi_1^\alpha \mid G_1^\alpha \mid \psi_2^\gamma \rangle - \epsilon_2^\alpha \langle \psi_2^\alpha \mid \psi_0 \rangle - \epsilon_2^\alpha \langle \psi_1^\alpha \mid \psi_1^\alpha \rangle - 2\epsilon_1^\alpha \langle \psi_1^\alpha \mid \psi_0 \rangle; \qquad (6)$$

$$\begin{aligned} \epsilon_{11}^{\alpha\beta} = {} & 2\langle \psi_2^\alpha \mid G_1^\beta \mid \psi_1^\alpha \rangle + 2\langle \psi_2^\alpha \mid G_1^\alpha \mid \psi_1^\beta \rangle - 2\epsilon_2^\alpha \langle \psi_1^\beta \mid \psi_1^\beta \rangle - 2\epsilon_{11}^{\alpha\beta} \langle \psi_2^\alpha \mid \psi_0 \rangle \\ & - \epsilon_{11}^{\alpha\beta} \langle \psi_1^\alpha \mid \psi_1^\alpha \rangle - 2\epsilon_3^\alpha \langle \psi_1^\beta \mid \psi_0 \rangle - 2\epsilon_{21}^{\alpha\beta} \langle \psi_1^\alpha \mid \psi_0 \rangle; \end{aligned} \qquad (7)$$

$$\begin{aligned} \epsilon_{22}^{\alpha\beta} = {} & -2\langle \psi_2^\alpha \mid G_0 \mid \psi_2^\beta \rangle - \langle \psi_{11}^{\alpha\beta} \mid G_0 \mid \psi_{11}^{\alpha\beta} \rangle - \epsilon_2^\alpha \langle \psi_1^\beta \mid \psi_1^\beta \rangle - \epsilon_2^\beta \langle \psi_1^\alpha \mid \psi_1^\alpha \rangle \\ & - 2\epsilon_{11}^{\alpha\beta} \langle \psi_1^\alpha \mid \psi_1^\beta \rangle - 2\epsilon_{21}^{\alpha\beta} \langle \psi_1^\beta \mid \psi_0 \rangle - 2\epsilon_{21}^{\beta\alpha} \langle \psi_1^\alpha \mid \psi_0 \rangle; \end{aligned} \qquad (8)$$

$$\begin{aligned} \epsilon_{211}^{\alpha\beta\gamma} = {} & -2\langle \psi_{11}^{\alpha\beta} \mid G_1^\alpha \mid \psi_1^\gamma \rangle + 2\langle \psi_{11}^{\alpha\beta} \mid G_1^\gamma \mid \psi_1^\alpha \rangle - 2\epsilon_{11}^{\alpha\gamma} \langle \psi_{11}^{\alpha\beta} \mid \psi_0 \rangle + 2\langle \psi_2^\alpha \mid G_1^\beta \mid \psi_1^\gamma \rangle \\ & + 2\langle \psi_2^\alpha \mid G_1^\gamma \mid \psi_1^\beta \rangle - 2\epsilon_2^\alpha \langle \psi_1^\beta \mid \psi_1^\gamma \rangle - 2\epsilon_2^\alpha \langle \psi_1^\gamma \mid \psi_1^\beta \rangle - 2\epsilon_{11}^{\alpha\beta} \langle \psi_1^\gamma \mid \psi_1^\alpha \rangle - 2\epsilon_{11}^{\alpha\gamma} \langle \psi_1^\alpha \mid \psi_1^\beta \rangle \\ & - 2\epsilon_{11}^{\beta\gamma} \langle \psi_2^\alpha \mid \psi_0 \rangle - \epsilon_{11}^{\beta\gamma} \langle \psi_1^\alpha \mid \psi_1^\alpha \rangle - 2\epsilon_{21}^{\alpha\beta} \langle \psi_1^\gamma \mid \psi_0 \rangle - 2\epsilon_{21}^{\alpha\gamma} \langle \psi_1^\beta \mid \psi_0 \rangle - 2\epsilon_{111}^{\alpha\beta\gamma} \langle \psi_1^\alpha \mid \psi_0 \rangle; \end{aligned} \qquad (9)$$

$$\epsilon_5^{\alpha} - \langle\psi_2^{\alpha}|G_1^{\alpha}|\psi_2^{\alpha}\rangle - 2\epsilon_2^{\alpha}\langle\psi_2^{\alpha}|\psi_1^{\alpha}\rangle - 2\epsilon_3^{\alpha}\langle\psi_1^{\alpha}|\psi_0\rangle - 2\epsilon_4^{\alpha}\langle\psi_1^{\alpha}|\psi_0\rangle - \epsilon_3^{\alpha}\langle\psi_1^{\alpha}|\psi_1^{\alpha}\rangle; \quad (10)$$

$$\begin{aligned}\epsilon_{12}^{\alpha\beta} - 2\langle\psi_2^{\alpha}|G_1^{\beta}|\psi_{11}^{\alpha\beta}\rangle + 2\langle\psi_2^{\alpha}|G_1^{\alpha}|\psi_2^{\beta}\rangle + \langle\psi_{11}^{\alpha\beta}|G_1^{\alpha}|\psi_{11}^{\alpha\beta}\rangle - 2\epsilon_2^{\beta}\langle\psi_2^{\alpha}|\psi_1^{\alpha}\rangle \\ -2\epsilon_{11}^{\alpha\beta}\langle\psi_2^{\alpha}|\psi_1^{\beta}\rangle - 2\epsilon_{21}^{\beta\alpha}\langle\psi_2^{\alpha}|\psi_0\rangle - 2\epsilon_2^{\alpha}\langle\psi_{11}^{\alpha\beta}|\psi_1^{\beta}\rangle - 2\epsilon_{11}^{\alpha\beta}\langle\psi_{11}^{\alpha\beta}|\psi_1^{\alpha}\rangle \\ -2\epsilon_{21}^{\alpha\beta}\langle\psi_{11}^{\alpha\beta}|\psi_0\rangle - 2\epsilon_2^{\alpha}\langle\psi_2^{\beta}|\psi_1^{\alpha}\rangle - 2\epsilon_3^{\alpha}\langle\psi_2^{\beta}|\psi_0\rangle - \epsilon_3^{\alpha}\langle\psi_1^{\beta}|\psi_1^{\beta}\rangle - 2\epsilon_{21}^{\alpha\beta}\langle\psi_1^{\beta}|\psi_1^{\alpha}\rangle \\ -2\epsilon_{31}^{\alpha\beta}\langle\psi_1^{\beta}|\psi_0\rangle - \epsilon_{12}^{\alpha\beta}\langle\psi_1^{\alpha}|\psi_1^{\alpha}\rangle - 2\epsilon_{22}^{\alpha\beta}\langle\psi_1^{\alpha}|\psi_0\rangle;\end{aligned} \quad (11)$$

$$\begin{aligned}\epsilon_{41}^{\alpha\beta} - 2\langle\psi_2^{\alpha}|G_1^{\alpha}|\psi_{11}^{\alpha\beta}\rangle + \langle\psi_2^{\alpha}|G_1^{\beta}|\psi_2^{\alpha}\rangle - 2\epsilon_2^{\alpha}\langle\psi_2^{\alpha}|\psi_1^{\beta}\rangle - 2\epsilon_{11}^{\alpha\beta}\langle\psi_2^{\alpha}|\psi_1^{\alpha}\rangle \\ -2\epsilon_{21}^{\alpha\beta}\langle\psi_2^{\alpha}|\psi_0\rangle - 2\epsilon_2^{\alpha}\langle\psi_{11}^{\alpha\beta}|\psi_1^{\alpha}\rangle - 2\epsilon_3^{\alpha}\langle\psi_{11}^{\alpha\beta}|\psi_0\rangle - 2\epsilon_3^{\alpha}\langle\psi_1^{\alpha}|\psi_1^{\beta}\rangle \\ -2\epsilon_{31}^{\alpha\beta}\langle\psi_1^{\alpha}|\psi_0\rangle - 2\epsilon_4^{\alpha}\langle\psi_1^{\beta}|\psi_0\rangle - \epsilon_{21}^{\alpha\beta}\langle\psi_1^{\alpha}|\psi_1^{\alpha}\rangle;\end{aligned} \quad (12)$$

$$\begin{aligned}\epsilon_{311}^{\alpha\beta\gamma} - 2\langle\psi_2^{\alpha}|G_1^{\alpha}|\psi_{11}^{\beta\gamma}\rangle + 2\langle\psi_2^{\alpha}|G_1^{\beta}|\psi_{11}^{\alpha\gamma}\rangle + 2\langle\psi_2^{\alpha}|G_1^{\gamma}|\psi_{11}^{\alpha\beta}\rangle + 2\langle\psi_{11}^{\alpha\beta}|G_1^{\alpha}|\psi_{11}^{\beta\gamma}\rangle \\ -2\epsilon_{11}^{\alpha\beta}\langle\psi_2^{\alpha}|\psi_1^{\gamma}\rangle - 2\epsilon_{11}^{\alpha\gamma}\langle\psi_2^{\alpha}|\psi_1^{\beta}\rangle - 2\epsilon_{11}^{\beta\gamma}\langle\psi_2^{\alpha}|\psi_1^{\alpha}\rangle - 2\epsilon_{111}^{\alpha\beta\gamma}\langle\psi_2^{\alpha}|\psi_0\rangle - 2\epsilon_2^{\alpha}\langle\psi_{11}^{\alpha\beta}|\psi_1^{\gamma}\rangle \\ -2\epsilon_{11}^{\alpha\gamma}\langle\psi_{11}^{\alpha\beta}|\psi_1^{\alpha}\rangle - 2\epsilon_2^{\alpha}\langle\psi_{11}^{\alpha\gamma}|\psi_1^{\beta}\rangle - 2\epsilon_{11}^{\beta\gamma}\langle\psi_{11}^{\alpha\beta}|\psi_1^{\alpha}\rangle - 2\epsilon_{21}^{\alpha\beta}\langle\psi_1^{\alpha}|\psi_1^{\gamma}\rangle - 2\epsilon_{21}^{\alpha\gamma}\langle\psi_1^{\alpha}|\psi_1^{\beta}\rangle - 2\epsilon_{211}^{\alpha\beta\gamma}\langle\psi_1^{\alpha}|\psi_0\rangle \\ -2\epsilon_3^{\alpha}\langle\psi_1^{\beta}|\psi_1^{\gamma}\rangle - 2\epsilon_{31}^{\alpha\gamma}\langle\psi_1^{\beta}|\psi_0\rangle - 2\epsilon_{31}^{\alpha\beta}\langle\psi_1^{\gamma}|\psi_0\rangle - 2\epsilon_3^{\alpha}\langle\psi_{11}^{\beta\gamma}|\psi_0\rangle \\ -2\epsilon_{21}^{\alpha\gamma}\langle\psi_0|\psi_{11}^{\alpha\beta}\rangle - \epsilon_{111}^{\alpha\beta\gamma}\langle\psi_1^{\alpha}|\psi_1^{\alpha}\rangle;\end{aligned} \quad (13)$$

$$\begin{aligned}\epsilon_{2221}^{\alpha\beta\gamma} - 2\langle\psi_2^{\alpha}|G_1^{\beta}|\psi_{11}^{\beta\gamma}\rangle + 2\langle\psi_2^{\alpha}|G_1^{\gamma}|\psi_2^{\beta}\rangle + 2\langle\psi_{11}^{\alpha\beta}|G_1^{\alpha}|\psi_{11}^{\beta\gamma}\rangle + \langle\psi_{11}^{\alpha\beta}|G_1^{\gamma}|\psi_{11}^{\alpha\beta}\rangle \\ +2\langle\psi_{11}^{\alpha\beta}|G_1^{\beta}|\psi_{11}^{\alpha\gamma}\rangle + 2\langle\psi_{11}^{\alpha\gamma}|G_1^{\alpha}|\psi_2^{\beta}\rangle + 2\langle\psi_{11}^{\alpha\gamma}|G_1^{\gamma}|\psi_2^{\alpha}\rangle - 2\epsilon_{11}^{\beta\gamma}\langle\psi_2^{\alpha}|\psi_1^{\alpha}\rangle - 2\epsilon_{21}^{\alpha\gamma}\langle\psi_2^{\alpha}|\psi_1^{\beta}\rangle - 2\epsilon_{21}^{\beta\gamma}\langle\psi_2^{\alpha}|\psi_1^{\gamma}\rangle \\ -2\epsilon_{11}^{\alpha\beta}\langle\psi_{11}^{\alpha\beta}|\psi_1^{\gamma}\rangle - 2\epsilon_{11}^{\alpha\gamma}\langle\psi_{11}^{\alpha\beta}|\psi_1^{\beta}\rangle - 2\epsilon_{11}^{\beta\gamma}\langle\psi_{11}^{\alpha\beta}|\psi_1^{\alpha}\rangle - 2\epsilon_{111}^{\alpha\beta\gamma}\langle\psi_{11}^{\alpha\beta}|\psi_0\rangle - 2\epsilon_2^{\beta}\langle\psi_{11}^{\alpha\gamma}|\psi_1^{\alpha}\rangle \\ -2\epsilon_{11}^{\alpha\beta}\langle\psi_{11}^{\alpha\gamma}|\psi_1^{\beta}\rangle - 2\epsilon_{21}^{\beta\alpha}\langle\psi_{11}^{\alpha\gamma}|\psi_0\rangle - 2\epsilon_2^{\alpha}\langle\psi_2^{\beta}|\psi_1^{\gamma}\rangle - 2\epsilon_{11}^{\alpha\gamma}\langle\psi_2^{\beta}|\psi_1^{\alpha}\rangle - 2\epsilon_{21}^{\alpha\gamma}\langle\psi_2^{\beta}|\psi_1^{\alpha}\rangle \\ -2\epsilon_{111}^{\alpha\beta\gamma}\langle\psi_1^{\beta}|\psi_1^{\alpha}\rangle - 2\epsilon_2^{\alpha}\langle\psi_{11}^{\beta\gamma}|\psi_1^{\alpha}\rangle - 2\epsilon_{21}^{\alpha\beta}\langle\psi_1^{\beta}|\psi_1^{\gamma}\rangle - \epsilon_{21}^{\alpha\gamma}\langle\psi_1^{\beta}|\psi_1^{\beta}\rangle \\ -2\epsilon_{211}^{\alpha\beta\gamma}\langle\psi_1^{\beta}|\psi_0\rangle - 2\epsilon_{12}^{\alpha\beta}\langle\psi_1^{\gamma}|\psi_1^{\alpha}\rangle - 2\epsilon_{22}^{\alpha\beta}\langle\psi_1^{\gamma}|\psi_0\rangle - 2\epsilon_{11}^{\alpha\beta}\langle\psi_1^{\beta\gamma}|\psi_1^{\alpha}\rangle \\ -2\epsilon_{21}^{\alpha\beta}\langle\psi_{11}^{\beta\alpha}|\psi_0\rangle - 2\epsilon_{121}^{\alpha\beta\gamma}\langle\psi_0|\psi_1^{\alpha}\rangle - \epsilon_{21}^{\beta\gamma}\langle\psi_1^{\alpha}|\psi_1^{\alpha}\rangle.\end{aligned} \quad (14)$$

These results assure that at nth order the wave functions and energy coefficients cannot involve more than p electrons and q centers at a time where p+q=n+2. This in turn means that at most n+1 electrons can be correlated at nth order while the greatest number of centers involved in an nth order coefficient is also n+1.

IV. Discussion

To calculate the second-order correction in the energy we need the first-order correction in the wave function Φ_1^a. The wave function Φ_1^a is obtained by the variational perturbation method, yielding an upper bound to the corresponding energy $\mathcal{E}_2^a$

$$e_2^a \le \langle \phi_1^a | G_0 | \phi_1^a \rangle + 2 \langle \phi_1^a | G_1 | \psi_0 \rangle .$$

Substitution of Φ_1^a into Eqn. (1) through (6) in Appendix (B) yields estimates of all energy coefficients complete through third order.

The second-order wave function can be obtained using the variational method, yielding an upper bound to the corresponding energy $\mathcal{E}_4^a$

$$e_4^a \le \langle \phi_2^a | G_0 | \phi_2^a \rangle + 2 \langle \phi_2^a | G_1^a | \psi_1^a \rangle - 2e_2^a \langle \phi_2^a | \psi_0 \rangle - e_2^a \langle \psi_1^a | \psi_1^a \rangle - 2e_1^a \langle \psi_1^a | \psi_0 \rangle .$$

Optimization of the second-order wave function (Φ_2^{α}) and the mixed wave function ($\Phi_{11}^{\alpha\beta}$) gives an upper bound to the $\mathcal{E}_2^{\alpha\beta}$ and $\mathcal{E}_{22}^{\alpha\beta}$, respectively, as well as estimates of the energy coefficients $\mathcal{E}_{31}^{\alpha\beta}$, $\mathcal{E}_{211}^{\alpha\beta\gamma}$, $\mathcal{E}_{32}^{\alpha\beta}$, $\mathcal{E}_{41}^{\alpha\beta}$, $\mathcal{E}_{311}^{\alpha\beta}$, and $\mathcal{E}_{221}^{\alpha\beta}$

$$\epsilon_{22}^{\alpha\beta} \le \langle\phi_{11}^{\alpha\beta}|G_0|\psi_{11}^{\alpha\beta}\rangle + 2\langle\phi_{11}^{\alpha\beta}|G_1^{\alpha}|\psi_1^{\beta}\rangle + 2\langle\phi_{11}^{\alpha\beta}|G_1^{\beta}|\psi_1^{\alpha}\rangle - 2\epsilon_{11}^{\alpha\beta}\langle\phi_{11}^{\alpha\beta}|\psi_0\rangle - 2\langle\psi_2^{\alpha}|G_0|\psi_2^{\beta}\rangle - \epsilon_2^{\alpha}\langle\psi_1^{\beta}|\psi_1^{\beta}\rangle - 2\epsilon_{11}^{\alpha\beta}\langle\psi_1^{\alpha}|\psi_1^{\beta}\rangle - \epsilon_2^{\beta}\langle\psi_1^{\alpha}|\psi_1^{\alpha}\rangle - 2\epsilon_{21}^{\alpha\beta}\langle\psi_1^{\beta}|\psi_0\rangle - 2\epsilon_{21}^{\beta\alpha}\langle\psi_1^{\alpha}|\psi_0\rangle .$$

In the multiperturbation theory , the lowest-order wave functions for a polyatomic molecule are not only independent of the nuclear charges, but are also indpendent of the total number of nuclear centers and electrons for the molecule. Thus the complexity of the problem can be restricted to a manageable level determined by the highest order of the calculation. With the present choice of H0, 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.

It is found that the perturbation energy summed through second order generally yields results comparable in accuracy to Hartree-Fock values;[7,8] while the third and fourth-order values are comparable in accuracy to variational calculations of moderate complexity.[7] In order to improve the calculations, we have derived the fifth-order correction in the energy for polyatomic molecules.

Appendix (A)

Expressions for the multiperturbation differential equations are presented below :

$$G_0\psi_0 - 0 ; \tag{1}$$

$$G_0\psi_1^{\alpha} + G_1^{\alpha}\psi_0 - 0 ; \tag{2}$$

$$G_0\psi_2^{\alpha} + G_1^{\alpha}\psi_1^{\alpha} - \epsilon_2^{\alpha}\psi_0 - 0 ; \tag{3}$$

$$G_0\psi_{11}^{\alpha\beta} + G_1^{\alpha}\psi_1^{\beta} + G_1^{\beta}\psi_1^{\alpha} - \epsilon_{11}^{\alpha\beta}\psi_0 - 0 ; \tag{4}$$

$$G_0\psi_3^{\alpha} + G_1^{\alpha}\psi_2^{\alpha} - \epsilon_2^{\alpha}\psi_1^{\alpha} - \epsilon_3^{\alpha}\psi_0 - 0 ; \tag{5}$$

$$G_0\psi_{21}^{\alpha\beta} + G_1^{\alpha}\psi_{11}^{\alpha\beta} + G_1^{\beta}\psi_2^{\alpha} - \epsilon_2^{\alpha}\psi_1^{\beta} - \epsilon_{11}^{\alpha\beta}\psi_1^{\alpha} - \epsilon_{21}^{\alpha\beta}\psi_0 - 0 ; \tag{6}$$

$$G_0\psi_{111}^{\alpha\beta\gamma} + G_1^{\alpha}\psi_{11}^{\beta\gamma} + G_1^{\beta}\psi_{11}^{\alpha\gamma} + G_1^{\gamma}\psi_{11}^{\alpha\beta} - \epsilon_{11}^{\alpha\beta}\psi_1^{\gamma} - \epsilon_{11}^{\alpha\gamma}\psi_1^{\beta} - \epsilon_{11}^{\beta\gamma}\psi_1^{\alpha} - \epsilon_{111}^{\alpha\beta\gamma}\psi_0 - 0 ; \tag{7}$$

$$G_0\psi_4^{\alpha} + G_1^{\alpha}\psi_3^{\alpha} - \epsilon_2^{\alpha}\psi_2^{\alpha} - \epsilon_3^{\alpha}\psi_1^{\alpha}\psi_2^{\alpha}\epsilon_4^{\alpha}\psi_0 - 0 ; \tag{8}$$

$$G_0\psi_{22}^{\alpha\beta} + G_1^{\alpha}\psi_{12}^{\alpha\beta} + G_1^{\beta}\psi_{21}^{\alpha\beta} - \epsilon_2^{\alpha}\psi_2^{\beta} - \epsilon_2^{\beta}\psi_2^{\alpha} - \epsilon_{21}^{\alpha\beta}\psi_1^{\beta} - \epsilon_{12}^{\alpha\beta}\psi_1^{\alpha} - \epsilon_{11}^{\alpha\beta}\psi_{11}^{\alpha\beta} - \epsilon_{22}^{\alpha\beta}\psi_0 - 0 ; \tag{9}$$

$$G_0\psi_{31}^{\alpha\beta} + G_1^{\alpha}\psi_{21}^{\alpha\beta} + G_1^{\beta}\psi_3^{\alpha} - \epsilon_2^{\alpha}\psi_{11}^{\alpha\beta} - \epsilon_3^{\alpha}\psi_1^{\beta} - \epsilon_{21}^{\alpha\beta}\psi_1^{\alpha} - \epsilon_{11}^{\alpha\beta}\psi_2^{\alpha} - \epsilon_3^{\alpha\beta}\psi_0 - 0 ; \tag{10}$$

$$\begin{aligned} G_0\psi_{211}^{\alpha\beta\gamma} + G_1^{\alpha}\psi_{111}^{\alpha\beta\gamma} + G_1^{\beta}\psi_{21}^{\alpha\gamma} + G_1^{\gamma}\psi_{21}^{\alpha\beta} - \epsilon_{111}^{\alpha\beta\gamma}\psi_1^{\alpha} - \epsilon_2^{\alpha}\psi_{11}^{\beta\gamma} - \epsilon_{21}^{\alpha\beta}\psi_1^{\gamma} - \epsilon_{21}^{\alpha\gamma}\psi_1^{\beta} \\ - \epsilon_{11}^{\alpha\beta}\psi_{11}^{\alpha\gamma} - \epsilon_{11}^{\alpha\gamma}\psi_{11}^{\alpha\beta} - \epsilon_{11}^{\beta\gamma}\psi_2^{\alpha} - \epsilon_{211}^{\alpha\beta\gamma}\psi_0 - 0 ; \end{aligned} \tag{11}$$

$$G_0\psi_5^{\alpha} + G_1^{\alpha}\psi_4^{\alpha} - \epsilon_2^{\alpha}\psi_3^{\alpha} - \epsilon_3^{\alpha}\psi_2^{\alpha} - \epsilon_4^{\alpha}\psi_1^{\alpha} - \epsilon_5^{\alpha}\psi_0 - 0 ; \tag{12}$$

$$G_0\psi_{41}^{\alpha\beta} + G_1^{\alpha}\psi_{31}^{\alpha\beta} + G_1^{\beta}\psi_4^{\alpha} - \epsilon_2^{\alpha}\psi_{21}^{\alpha\beta} - \epsilon_3^{\alpha}\psi_{11}^{\alpha\beta} - \epsilon_{21}^{\alpha\beta}\psi_2^{\alpha} - \epsilon_{31}^{\alpha\beta}\psi_1^{\alpha} - \epsilon_4^{\alpha}\psi_1^{\beta} - \epsilon_{11}^{\alpha\beta}\psi_3^{\alpha} - \epsilon_{41}^{\alpha\beta}\psi_0 - 0 ; \tag{13}$$

$$\begin{aligned} G_0\psi_{32}^{\alpha\beta} + G_1^{\alpha}\psi_{22}^{\alpha\beta} + G_1^{\beta}\psi_{31}^{\alpha\beta} - \epsilon_2^{\alpha}\psi_{12}^{\alpha\beta} - \epsilon_2^{\beta}\psi_3^{\alpha} - \epsilon_3^{\alpha}\psi_2^{\beta} - \epsilon_{22}^{\alpha\beta}\psi_1^{\alpha} - \epsilon_{21}^{\alpha\beta}\psi_{11}^{\alpha\beta} - \epsilon_{12}^{\alpha\beta}\psi_2^{\alpha} - \epsilon_{31}^{\alpha\beta}\psi_1^{\beta} \\ - \epsilon_{11}^{\alpha\beta}\psi_{21}^{\alpha\beta} - \epsilon_{32}^{\alpha\beta}\psi_0 - 0 ; \end{aligned} \tag{14}$$

$$\begin{aligned} G_0\psi_{311}^{\alpha\beta\gamma} + G_1^{\alpha}\psi_{211}^{\beta\gamma} + G_1^{\beta}\psi_{31}^{\alpha\gamma} + G_1^{\gamma}\psi_{31}^{\alpha\beta} - \epsilon_{111}^{\alpha\beta\gamma}\psi_2^{\alpha} - \epsilon_2^{\alpha}\psi_{111}^{\beta\gamma} - \epsilon_{211}^{\alpha\beta\gamma}\psi_1^{\alpha} - \epsilon_3^{\alpha}\psi_{11}^{\beta\gamma} \\ - \epsilon_{21}^{\alpha\beta}\psi_{11}^{\alpha\gamma} - \epsilon_{21}^{\alpha\gamma}\psi_{11}^{\alpha\beta} - \epsilon_{31}^{\alpha\beta}\psi_1^{\gamma} - \epsilon_{31}^{\alpha\gamma}\psi_1^{\beta} - \epsilon_{11}^{\alpha\beta}\psi_{21}^{\alpha\gamma} - \epsilon_{11}^{\alpha\gamma}\psi_{21}^{\alpha\beta} - \epsilon_{11}^{\beta\gamma}\psi_3^{\alpha} - \epsilon_{311}^{\alpha\beta\gamma}\psi_0 - 0 ; \end{aligned} \tag{15}$$

$$\begin{aligned} G_0\psi_{221}^{\alpha\beta\gamma} + G_1^{\alpha}\psi_{121}^{\alpha\beta\gamma} + G_1^{\beta}\psi_{211}^{\alpha\beta\gamma} + G_1^{\gamma}\psi_{22}^{\alpha\beta} - \epsilon_{111}^{\alpha\beta\gamma}\psi_{11}^{\alpha\beta} - \epsilon_2^{\alpha}\psi_{21}^{\beta\gamma} - \epsilon_2^{\beta}\psi_{21}^{\alpha\gamma} - \epsilon_{211}^{\alpha\beta\gamma}\psi_1^{\beta} - \epsilon_{121}^{\alpha\beta\gamma}\psi_1^{\alpha} \\ - \epsilon_{22}^{\alpha\beta}\psi_1 - \epsilon_{21}^{\alpha\beta}\psi_{11}^{\beta\gamma} - \epsilon_{21}^{\alpha\gamma}\psi_2^{\beta} - \epsilon_{21}^{\beta\gamma}\psi_2^{\alpha} - \epsilon_{12}^{\alpha\beta}\psi_{11}^{\alpha\gamma} - \epsilon_{11}^{\alpha\beta}\psi_{111}^{\alpha\beta\gamma} - \epsilon_{11}^{\alpha\gamma}\psi_{12}^{\alpha\beta} - \epsilon_{11}^{\beta\gamma}\psi_{21}^{\alpha\beta} - \epsilon_{221}^{\alpha\beta\gamma}\psi_0 - 0 ; \end{aligned} \tag{16}$$

Where $G_0 = H_0 - \epsilon_0$ and $G_1^{\alpha} = H_1^{\alpha} - \epsilon_1^{\alpha}$

Appendix (B)

The third-order energy coefficients are presented below :

$$\epsilon_1^{\alpha} = \langle \psi_0 | H_1^{\alpha} | \psi_0 \rangle ; \tag{1}$$

$$\epsilon_2^{\alpha} = \langle \psi_1^{\alpha} | G_1^{\alpha} | \psi_0 \rangle ; \tag{2}$$

$$\epsilon_{11}^{\alpha\beta} = \langle \psi_1^{\alpha} | G_1^{\beta} | \psi_0 \rangle + \langle \psi_1^{\beta} | G_1^{\alpha} | \psi_0 \rangle ; \tag{3}$$

$$\epsilon_3^{\alpha} = \langle \psi_1^{\alpha} | G_1^{\alpha} | \psi_1^{\alpha} \rangle - 2\epsilon_2^{\alpha} \langle \psi_1^{\alpha} | \psi_0 \rangle ; \tag{4}$$

$$\epsilon_{21}^{\alpha\beta} = \langle \psi_1^{\alpha} | G_1^{\beta} | \psi_1^{\alpha} \rangle + 2 \langle \psi_1^{\alpha} | G_1^{\alpha} | \psi_1^{\beta} \rangle - 2\epsilon_{11}^{\alpha\beta} \langle \psi_1^{\alpha} | \psi_0 \rangle - 2\epsilon_2^{\alpha} \langle \psi_1^{\beta} | \psi_0 \rangle ; \tag{5}$$

$$\begin{aligned} \epsilon_{111}^{\alpha\beta\gamma} = {} & 2 \langle \psi_1^{\alpha} | G_1^{\beta} | \psi_1^{\gamma} \rangle + 2 \langle \psi_1^{\alpha} | G_1^{\gamma} | \psi_1^{\beta} \rangle + 2 \langle \psi_1^{\beta} | G_1^{\alpha} | \psi_1^{\gamma} \rangle - 2\epsilon_{11}^{\alpha\beta} \langle \psi_1^{\gamma} | \psi_0 \rangle \\ & - 2\epsilon_{11}^{\alpha\gamma} \langle \psi_1^{\beta} | \psi_0 \rangle - 2\epsilon_{11}^{\beta\gamma} \langle \psi_1^{\alpha} | \psi_0 \rangle ; \end{aligned} \tag{6}$$

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