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Calculation of Ground-State Energy for Linear HeH_2^{++} Through Fifth Order (United Atom Treatment)

حساب طاقة الحالة الأرضية للجزيء الخطي HeH_2^{++} حتى الدرجة الخامسة (معالجة الذرة المتحدة)

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Abstract

In this paper, the nonrelativistic energies of the linear HeH_2^{++} molecular ion have been computed using the multiperturbation theory for the ground state through fifth order. The results are very encouraging compared to the variational calculations.

في هذه الورقة , تم حساب الطاقات غير النسبية للجزيء الأيوني الخطي HeH_2^{++} باستخدام النظرية المتعددة القلقلة للحالة الأرضية حتى الدرجة الخامسة. كانت النتائج مشجعة جداً مقارنةً بالحسابات المبنية على أساس طريقة التغيير .

I. Introduction

A multiperturbation method has been proposed for the calculation of the energies of molecular systems through fourth and fifth order in the energy [1,2]. The techniques involved have been developed to the point that accurate energies can be obtained for small molecular systems [3].

The united atom treatment [4] of molecules is used for examining the behavior of the potential energy function for small values of internuclear distances. In the united-atom perturbation treatment of molecules [5,6] the unperturbed system is taken as the united atom, which corresponds to the molecule in question.

Chisholm and Lodge [7,8,9] have carried out the calculations for two-electron diatomic systems ($\mathbf{H_2}, \mathbf{HeH^+}, \mathbf{He^{++}}$) through second-order in the energy. Galvan, Abu-Jafar and Sanders [3] have studied the two-electron polyatomic systems ($\mathbf{HeH_2^{++}}$, $\mathbf{H_3^+}$) through third-order in the energy. The purpose of this paper is to extend the application of perturbation theory to fifth order in the energy and to the treatment of hetronuclear linear triatomic molecule $\mathbf{HeH_2^{++}}$.

II. Wave Functions

The zero-order wave function for this system is a properly symmetrized product of one - electron (hydrogenic) orbitals.

The first - order correction to the wave function is given by

$$\Psi_1 = \Psi_1^A(\vec{r}_1,\vec{r}_2) + Z_B\left[\Psi_1^m(R_B,\vec{r}_1)1s(\vec{r}_2) + 1s(\vec{r}_1)\Psi_1^m(R_B,\vec{r}_2)\right.$$

$$\left. + Z_C\left[\Psi_1^{m'}(R_C,\vec{r}_1)1s(\vec{r}_2) + 1s(\vec{r}_1)\Psi_1^{m'}(R_C,\vec{r}_2)\right]\right], \qquad (1)$$

where R_B and R_c are the internuclear distances between the charge Z_A and the two perturbing charges, Z_B and Z_c, respectively. The angle subtended by these two perturbing charges is denoted by θ.

The charge Z_A is chosen as the largest of the nuclear charges in the linear molecule $\mathbf{HeH_2^{++}}$ on which the electrons are centered. Ψ_1^A and Ψ_1^m are the first - order corrections in the atomic and molecular wave functions, respectively.

The multicenter integrals appear in the energy expansion coefficients. In order to simplify the evaluation of these integrals, the single-center basis sets have been used for all wave functions.

The first - order correction in the atomic wave function is given by

$$\Psi_1^A(\vec{r}_1,\vec{r}_2)=\sum_{i=1}^{N} C_i^{\mathrm{A}}\,\phi_i \ , \tag{2}$$

where the coefficients C_i^{A} are chosen to minimize the computed total energy. Hence

$$\Psi_1^{\mathrm{A}}=\sum_{i=1}^{N}\left(1+P_{12}\right)C_i^{\mathrm{A}}\, r_1^n r_2^m P_l(\cos\theta_{12})e^{-k_\ell(\vec{r}_1+\vec{r}_2)} \ , \tag{3}$$

where P_{12} is the operator which interchanges the subscripts 1 and 2 , and θ_{12} is the angle between $\vec{r}_1$ and $\vec{r}_2$. The nonlinear parameter k_ℓ is optimized by the variational - perturbation method.

For the atomic wave function, all terms with $\ell \le 16$ and $n+m+2\ell \le 20$ have been included with a total of 501 terms.

The first- order correction in the molecular wave function is given by

$$\Psi_1^m(R,\vec{r}_i)=\sum_{i=1}^{N} C_i^m\,\phi_i(R,\vec{r}_i)$$

$$=\sum_{i=1}^{N} C_i^m\, r_i^n P_\ell(\cos\theta_i)e^{-\beta_\ell r_i} \ , \tag{4}$$

where C_i^m are coefficients optimized variationally. The nonlinear parameter β_1 is also optimized variationally.

For the molecular wave function, all terms with $\ell \le 16$ and $\ell + n \le 20$ have been used with a total of 221 terms.

The second - order correction to the wave function is given by

$$\Psi_2=\Psi_2^{\mathrm{A}}(\vec{r}_1,\vec{r}_2)+Z_B^2\left[\Psi_2^m(R_B,\vec{r}_1)1s(\vec{r}_2)+1s(\vec{r}_1)\Psi_2^m(R_B,\vec{r}_2)\right]+Z_C^2\left[\Psi_2^{m'}(R_C,\vec{r}_1)1s(\vec{r}_2)\right.$$

$$+1s(\vec{r}_1)\Psi_2^{m'}(R_C,\vec{r}_2)\Big]+Z_BZ_C\Big[\Psi_{11}^{mm'}(R_B,R_C,\theta,\vec{r}_1)1s(\vec{r}_2)+1s(\vec{r}_1)\Psi_{11}^{mm'}(R_B,R_C,\theta,\vec{r}_2)\Big]$$
$$+Z_B\Psi_{11}^{Am}(R_B,\vec{r}_1,\vec{r}_2)+Z_C\Psi_{11}^{Am'}(R_C,\vec{r}_1,\vec{r}_2) \quad (5)$$

ψ_1^A and ψ_2^A can be obtained from variational-perturbation calculations [10].

ψ_1^m and ψ_2^m are known in a closed form [11,12]. The ψ_{11} wave functions are obtained by a multiperturbation variant of the variational-perturbation method, yielding upper bounds to the corresponding ε_{22} in the process.

ψ_2^A and ψ_{11}^{Am} all utilize the same basis set for the trial wave functions

$$(1+P_{12})\sum_{\ell mn}C_{\ell mn}r_1^n r_2^m P_\ell(\cos\theta_{12})\exp[-k_\ell(\vec{r}_1+\vec{r}_2)] \ .$$

Similarly, ψ_2^m and $\psi_{11}^{mm'}$ both utilize the basis

$$\sum_{n\ell}C_{\ell n}r_i^n P_\ell(\cos\theta_i)\exp(-\beta_\ell r_i) \ .$$

III. Method

The multiperturbation theory has been thoroughly discussed in scientific articles [1,2,3]. For the HeH_2^{++} molecular ion, we have two electrons and three nuclei of charges Z_A, Z_B and Z_c.

The total Hamiltonian of the HeH_2^{++} system in charge-scaled atomic units can be written as

$$H = H_0 + H_1, \quad (6)$$

where $\mathbf{H_0}$ is the unperturbed Hamiltonian and the perturbation $\mathbf{H_1}$ is given by

$$H_1 = \lambda_A H_1^{A} + \lambda_m H_1^{m} + \lambda_{m'} H_1^{m'} \quad . \tag{7}$$

$\mathbf{H_0}$ can be written in scaled a.u. as

$$H_0 \equiv -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{1}{r_{1A}} - \frac{1}{r_{2A}} \quad . \tag{8}$$

The perturbation H_1^{A} is the electron - electron interaction:

$$H_1^{A} = \frac{1}{r_{12}}, \tag{9}$$

and $\lambda_A \equiv \dfrac{1}{Z_A}$ is the inverse of the nuclear charge.

The perturbation H_1^{m} is the electron - nuclear interaction:

$$H_1^{m} = -\left(\frac{1}{r_{1B}} + \frac{1}{r_{2B}}\right), \tag{10}$$

and $\lambda_m \equiv \dfrac{Z_B}{Z_A}$ is the ratio of the nuclear charges.

The perturbation $H_1^{m'}$ is given by

$$H_1^{m'} = -\left(\frac{1}{r_{1C}} + \frac{1}{r_{2C}}\right), \tag{11}$$

and $\lambda m' \dfrac{Z_C}{Z_A}$.

The expressions for the multiperturbation energy - expansion coefficients through fifth order are derived by Abu-Jafar et al. [2].

The first - order energy coefficient for the ground state of the molecule is

$$\varepsilon_1 = \varepsilon_1^A + 2 Z_B \varepsilon_1^m(R_B) + 2 Z_C \varepsilon_1^m(R_C). \tag{12}$$

The first- order correction to the ground state energy of a two - electron atom is $\varepsilon_1^A = 5/8$. On the other hand, the first-order correction to the ground state energy of a one - electron diatomic molecule with internuclear distance R is given by

$$\varepsilon_1^m(R) = -\frac{1}{R} + \left(1 + \frac{1}{R}\right) e^{-2R} \tag{13}$$

With the use of wave function ψ_1, one can calculate the second - and third - order energy coefficients.

The second - order energy is given by

$$\varepsilon_2 = \varepsilon_2^A + 2 Z_B^2 \varepsilon_2^m(R_B) + 2 Z_C^2 \varepsilon_2^{m'}(R_C) + Z_B \varepsilon_1^{Am}(R_B) + Z_C \varepsilon_1^{Am'}(R_C) + 2 Z_B Z_C \varepsilon_1^{mm'}(R_B, R_C, \theta), \tag{14}$$

where $\varepsilon_2^A = -0.1576664$ [10], ε_2^m is known exactly [11], and ε_{11}^{Am} has been derived by Chisholm and Lodge [9]. Note that the dependence of the energy on the angle θ first appears in this order through the term $\varepsilon_{11}^{mm'}$ [3].

The third-order energy can also be obtained from the first-order wave function ψ_1 and is given by

$$\begin{aligned}\varepsilon_3 = {} & \varepsilon_3^A + 2 Z_B^3 \varepsilon_3^m(R_B) + 2 Z_C^3 \varepsilon_3^{m'}(R_C) + Z_B \varepsilon_{21}^{Am}(R_B) + Z_C \varepsilon_{21}^{Am'}(R_C) + Z_B^2 \varepsilon_{12}^{Am}(R_B) \\ & + Z_C^2 \varepsilon_{12}^{Am'}(R_C) + 2 Z_B^2 Z_C \varepsilon_{21}^{mm'}(R_B, R_C, \theta) + 2 Z_B Z_C^2 \varepsilon_{12}^{mm'}(R_B, R_C, \theta) \\ & + Z_B Z_C \varepsilon_{111}^{Amm'}(R_B, R_C, \theta)\end{aligned} \tag{15}$$

Several of the above coefficients are either known exactly or are obtained from variational calculations. The remaining coefficients can be computed from the first - order wave functions.

With the use of wave function ψ_2, one can calculate the fourth - and fifth - order energy coefficients.

The fourth - order energy is given by

$$\begin{aligned}\varepsilon_4 &= \varepsilon_4^A + 2Z_B^4\varepsilon_4^{m'}(R_B) + 2Z_C^4\varepsilon_4^{m'}(R_C) + Z_BZ_C\varepsilon_{31}^{Am'}(R_B) + Z_BZ_C\varepsilon_{31}^{Am'}(R_C) + Z_B^2\varepsilon_{22}^{Am'}(R_B) + Z_C^2\varepsilon_{22}^{Am'}(R_C) \\ &+ Z_B^3\varepsilon_{13}^{Am'}(R_B) + Z_C^3\varepsilon_{13}^{Am'}(R_C) + 2Z_B^3Z_C\varepsilon_{31}^{mm'}(R_B,R_C,\theta) + 2Z_B^2Z_C^2\varepsilon_{22}^{mm'}(R_B,R_C,\theta) \\ &+ 2Z_BZ_C^3\varepsilon_{13}^{mm'}(R_B,R_C,\theta) + Z_BZ_C\varepsilon_{211}^{Amm'}(R_B,R_C,\theta) + Z_B^2Z_C\varepsilon_{121}^{Amm'}(R_B,R_C,\theta) \\ &+ Z_BZ_C^2\varepsilon_{112}^{Amm'}(R_B,R_C,\theta) \end{aligned} \quad (16)$$

The fifth - order energy is given by

$$\begin{aligned}\varepsilon_5 &= \varepsilon_5^A + 2Z_B^5\varepsilon_5^{m'}(R_B) + 2Z_C^5\varepsilon_5^{m'}(R_C) + Z_B^2\varepsilon_{32}^{Am'}(R_B) + Z_C^2\varepsilon_{32}^{Am'}(R_C) + Z_B^3\varepsilon_{23}^{Am'}(R_B) \\ &+ Z_C^3\varepsilon_{23}^{Am'}(R_C) + Z_B^4\varepsilon_{14}^{Am'}(R_B) + Z_C^4\varepsilon_{14}^{Am'}(R_C) + Z_B\varepsilon_{41}^{Am'}(R_B) + Z_C\varepsilon_{41}^{Am'}(R_C) \\ &+ 2Z_B^3Z_C^2\varepsilon_{32}^{mm'}(R_B,R_C,\theta) + 2Z_B^2Z_C^3\varepsilon_{23}^{mm'}(R_B,R_C,\theta) + 2Z_B^4Z_C\varepsilon_{41}^{mm'}(R_B,R_C,\theta) \\ &+ 2Z_BZ_C^4\varepsilon_{14}^{mm'}(R_B,R_C,\theta) + Z_BZ_C\varepsilon_{311}^{Amm'}(R_B,R_C,\theta) + Z_B^3Z_C\varepsilon_{131}^{Amm'}(R_B,R_C,\theta) \\ &+ Z_BZ_C^3\varepsilon_{113}^{Amm'}(R_B,R_C,\theta) + Z_B^2Z_C\varepsilon_{221}^{Amm'}(R_B,R_C,\theta) + Z_BZ_C^2\varepsilon_{212}^{Amm'}(R_B,R_C,\theta) \\ &+ Z_B^2Z_C^2\varepsilon_{122}^{Amm'}(R_B,R_C,\theta) \end{aligned} \quad (17)$$

With the exception of the singly - subscripted coefficients, most of the above coefficients in eqs. (16 & 17) have been calculated here directly from the appropriate components of the second - order wave function.

The total energy through fifth - order for this molecular ion, in ordinary atomic units, is then given by

$$\mathbf{E} = \sum_{m=0}^{5} Z^{2-m} \varepsilon_m + \frac{Z_A Z_B}{R_B} + \frac{Z_A Z_C}{R_C} + \frac{Z_B Z_C}{R} \qquad (18)$$

Results for the third-, fourth-, and fifth-order perturbation sums of the energy for $\mathbf{HeH}_2^{++}$ are presented in Table 1 for $\theta = 180^0$, where they are also compared to the available variational calculations.

IV. Results and Discussion

There is no experimental evidence to show that the system $\mathbf{HeH}_2^{++}$ exists as a stable molecular ion, although $\mathbf{HeH}_2^{+}$ may be stable [13]. Zetik and Poshusta [14,15] have done the variational calculations over a wide range of internuclear distances for the $\mathbf{HeH}_2^{++}$ molecule. They have found that there is no internuclear equilibrium distance for this molecule.

Table I and Fig.1 present the total energy through fifth-order correction for $\mathbf{HeH}_2^{++}$. The total energies have been calculated for only the symmetric linear configuration of this molecule.

When compared to the results of Zetik and Poshusta [14,15], we find that $\varepsilon_3, \varepsilon_4$ *and* ε_5 all lie below variational calculations by roughly 0.05 a.u or so. One can only note the rapid convergence of the perturbation series produced here with a Z_A of 2; so that the contribution of ε_4 & ε_5 to the total energy is likely to be relatively small.

The improvement in convergence is true for heteronuclear molecules, especially for those with a single heavy ion.

We can see from Table I & Fig. 1 that this molecule does not have a minimum energy, which means that it does not appear as a bound system. Hence this molecule is unstable. The multiperturbation coefficients with two "molecular" perturbations as in $\mathbf{HeH}_2^{++}$ are small for large R. The significant contribution to $\varepsilon_3, \varepsilon_4$ *and* ε_5 at large R comes from $\varepsilon_3^A, \varepsilon_4^A$ *and* ε_5^A,

respectively. Therefore, we can conclude from this study that the ground state of linear $\mathbf{HeH}_2^{++}$ is not bound.

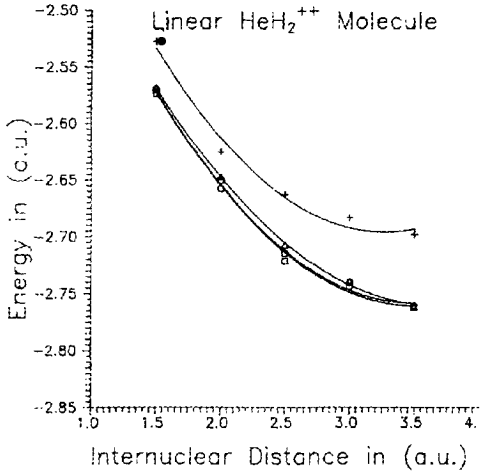
Finally, a computer program has been written in Fortran -77 in quadruple precision to compute the total energy E(R) for a given internuclear distance R, and this has been coupled to an optimizing routine to find the minimum of E(R).

Table 1. Total energies (in a.u) for the linear, symmetric HeH_2^{++} molecule $(\theta = 180^0)$; truncated energy sums $(\varepsilon_3, \varepsilon_4, \varepsilon_5)$ are compared to the variational results.

R (a.u.)	ε_3	ε_4	ε_5	ε(Variational)[a]
1.5	-2.564	-2.567	-2.565	-2.528
2.0	-2.664	-2.668	-2.662	-2.626
2.5	-2.710	-2.718	-2.708	-2.663
3.0	-2.739	-2.743	-2.740	-2.684
3.5	-2.762	-2.763	-2.761	-2.699

[a] Zetik and Poshusta [14,15].

Figure: 1. Energy for linear, symmetric HeH_2^{++} ; (O)ε_3; (■) ε_4; (Δ)ε_5; (+) variational results of Zetik and Pushusta [14,15].



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