

# Perturbation theory of the spatial confinement effects in the Rydberg HeH molecule

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## Abstract

The applicability of the perturbation theory to studies on the effect of confinement is discussed in the context of the influence of spatial confinement on the Rydberg HeH molecule. In the analysis the confining potential is assumed to have cylindrical symmetry, with symmetry axis of the potential overlapping with the molecular axis. In the direction perpendicular to the axis the quadratic dependence of the potential on the electron coordinates is assumed. The ionization due to the confinement and the influence of the confining potential on the form of the potential energy curves, in particular on the bond lengths, are studied in detail.

*Key words:* Rydberg molecules, confining potential

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## 1 Introduction

Confining potentials are frequently used to model the influence of environmental factors on properties of atoms and molecules, as for example the influence of plasma [1,2], of

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external magnetic fields [3], and of surfaces [4,5]. A review of the subject has been published a decade ago by Jaskólski [6]. More recent developments are covered in a paper by Connerade [7]. The influence of confining potentials on properties of atoms has recently been analyzed by several authors [8–10]. Among recent studies on confined molecules one should mention a detailed study of  $\text{H}_2$  confined by a spherical harmonic potential [11] and another study on  $\text{H}_3^+$  and  $\text{H}_2$  [12] in cylindrical confinement. The effects of a cylindrical confining potential on the excited states of the  $\text{H}_2$  molecule were investigated [13] and detailed studies of  $\text{Li}_2$  in anisotropic harmonic potentials are available [14].

In the present work the influence of cylindrical harmonic oscillator confinement on the  $\text{HeH}$  molecule is investigated. It is assumed that the molecular axis is parallel to the uniform external magnetic field.

The molecule belongs to the family of Rydberg molecules with an unstable ground state and bound excited states. The Rydberg electron is very sensitive to any kind of external perturbation. Therefore the effects of spatial confinement should be evident for relatively weak confinements, making them suitable for an analysis by perturbation theory.

The principal subject addressed in the present work is the applicability of perturbation theory for investigating the influence of confinement on molecular properties. While usually the studies have been performed using the configuration interaction method, the analysis of the results of the present work shows that perturbation theory may also be adequate for the description of the effects of confinement.

Further, the influence of the confining potential on the shape of the potential energy curves is studied in detail for the ground state and for the first four excited states of the  $\text{HeH}$  molecule. In addition, the values of the parameter defining the strength of the confinement by which the molecule in a given electronic state becomes ionized [7] are determined. These values of critical confinement parameters correspond to the strength of the external magnetic field causing the ionization [15]. The expressions for these parameters as functions of the internuclear distances are derived.

## 2 Theory

The Hamiltonian of the confined  $N$ -electron molecule is taken as

$$\hat{H}_\omega(\mathbf{r}, R) = \hat{H}_0(\mathbf{r}, R) + \mathcal{W}(\mathbf{r}), \quad (1)$$

where

$$\hat{H}_0(\mathbf{r}, R) = \hat{T}(\mathbf{r}) + \hat{V}(\mathbf{r}, R) + \hat{G}(\mathbf{r}) \quad (2)$$

is the Born-Oppenheimer Hamiltonian of the free system,  $\hat{T}(\mathbf{r})$ ,  $\hat{V}(\mathbf{r}, R)$ ,  $\hat{G}(\mathbf{r})$  represent, respectively, the  $N$ -electron operators describing the kinetic energy, the nuclear attraction potential, and the electron repulsion potential;  $\mathbf{r} \equiv \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$  stands for the electron coordinates and  $R$  denotes the internuclear distance. The  $N$ -electron confinement potential  $\mathcal{W}(\mathbf{r})$  is defined as a sum of one-electron contributions:

$$\mathcal{W}(\mathbf{r}) = \sum_{i=1}^N W(\mathbf{r}_i), \quad (3)$$

where  $\mathbf{r}_i = \{x_i, y_i, z_i\}$ .

In the present work the confining potential is taken as the cylindrical harmonic oscillator potential, i.e.

$$W(\mathbf{r}_i) = \frac{\omega^2}{2}(x_i^2 + y_i^2). \quad (4)$$

The molecular axis is chosen in such a way that it overlaps with the  $z$  axis of the coordinate system. In such case there is no confining potential along the molecular axis and, as a result, in this direction there is no interaction between the nuclei and the confinement. The interaction between the nuclei and the confinement in directions perpendicular to the molecular axis has been neglected in this work.

The confinement proportional to  $x^2 + y^2$  may model an external uniform magnetic field [15].

The energy of the electronic states of a confined HeH molecule increases with the increasing strength of the confinement faster than the ground state energy of the positive ion HeH<sup>+</sup>. Therefore, for each electronic state there exists a critical confinement parameter  $\omega_0$  beyond which the energy of the neutral molecule is larger than that of the ion. For confinements stronger than the critical confinement the corresponding electron is bound by the confining potential rather than by the nuclei and its energy spectrum is mainly determined by the form of the confinement. This behaviour of the energies is related to the phenomenon of *autoionization of atoms by pressure* [7] and was discovered already in the 1930s [16]. The theory developed in the present paper applies to the bound states only. Therefore the range of valid confinement parameters is determined by the inequality

$$0 < \omega < \omega_0. \quad (5)$$

As it is shown in the following sections, for the cases considered in the present work the critical confinement parameter  $\omega_0$  is much smaller than 1. For such cases, when  $\omega \ll 1$ , the effects of confinement may be studied using perturbation theory. The Schrödinger equation describing a molecule confined by a parabolic potential may be written as

$$\left[ \hat{H}_0(\mathbf{r}, R) + \omega^2 \hat{H}'(\mathbf{r}) \right] \Psi_\omega^n(\mathbf{r}, R) = E_\omega^n(R) \Psi_\omega^n(\mathbf{r}, R), \quad (6)$$

where

$$\hat{H}'(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^N (x_i^2 + y_i^2). \quad (7)$$

The zeroth order ( $\omega = 0.0$ ) wavefunction satisfies the eigenvalue equation of the Hamiltonian  $\hat{H}_0$ :

$$\hat{H}_0(\mathbf{r}, R)\Psi_0^n(\mathbf{r}, R) = E_0^n(R)\Psi_0^n(\mathbf{r}, R). \quad (8)$$

The perturbation expansion may be written as

$$E_\omega^n = E_0^n + E_I^n \omega^2 + E_{II}^n \omega^4 + \dots, \quad (9)$$

where

$$E_I^n = \langle \Psi_0^n | \hat{H}' | \Psi_0^n \rangle = \frac{1}{2} \sum_{i=1}^N \langle \Psi_0^n | x_i^2 + y_i^2 | \Psi_0^n \rangle. \quad (10)$$

### 3 Computational Method

In order to provide the reference solutions the electronic Schrödinger equation for the  $n$ -th electronic state

$$\hat{H}_\omega(\mathbf{r}, R)\Psi_\omega^n(\mathbf{r}, R) = E_\omega^n(R)\Psi_\omega^n(\mathbf{r}, R) \quad (11)$$

is solved by using the multireference configuration interaction method implemented in OpenMol [17] and GAMESS [18], using large Gaussian basis sets [19]. For several values of the confinement parameter  $\omega$ , the potential energy curves  $E_\omega^n(R)$ ,  $n = 0, 1, 2, 3, 4$ , (where  $n = 0$  denotes the ground state,  $n = 1$  the first excited,  $n = 2$  the second excited, and so on) of the HeH molecule as well as the potential energy curves  $E_\omega^{0+}(R)$  of the HeH<sup>+</sup> ion in the ground state were computed.

In the perturbation approximation of the effects of confinement on the potential energy curves the  $k$ -th order polynomial representation of the energy for the  $n$ -th state was constructed

$$\tilde{E}_{\omega,k}^n(R) = \sum_{i=0}^k C_{ki}^n(R)\omega^{2i}. \quad (12)$$

The quadratic approximation ( $k = 1$ ) corresponds to the first-order perturbation expansion. The fourth-order approximation ( $k = 2$ ) leads to the perturbation expansion up to the second order.

The zeroth order approximation to the energy of the confined molecule is chosen as the energy of the unconfined molecule, i.e. corresponding to  $\omega = 0.0$ ,

$$\tilde{E}_{\omega,0}^n(R) = C_{00}^n(R) = E_0^n(R) \quad (13)$$

[cf. Eq. (9)]. Let us define, for confinement parameters  $\omega_j \neq 0.0$ ,

$$\tilde{f}_k^n(\omega_j, R) = \frac{\tilde{E}_{\omega_j,k}^n(R) - E_0^n(R)}{\omega_j^2} \quad (14)$$

and

$$f^n(\omega, R) = \frac{E_\omega^n(R) - E_0^n(R)}{\omega^2}. \quad (15)$$

If  $E_\omega^n(R)$  and  $E_0^n(R)$  are known from MRCI calculations then the coefficients  $C_{ki}^n$  may be estimated using the least-square procedure:

$$\sum_{j=1}^J \left( f^n(\omega_j, R) - \tilde{f}_k^n(\omega_j, R) \right)^2 = \min. \quad (16)$$

For  $k = 1$  the condition for the minima leads to

$$\tilde{f}_1^n(\omega_j, R) = C_{11}^n(R) = \frac{X_0}{J}, \quad (17)$$

where

$$X_p = \sum_{j=1}^J f^n(\omega_j, R) \omega_j^{2p}, \quad p = 0, 1.$$

Analogously, for  $k = 2$ , the coefficients of the function

$$\tilde{f}_2^n(\omega_j, R) = C_{21}^n(R) + C_{22}^n(R) \omega_j^2$$

are

$$C_{21}^n(R) = \frac{X_0 Y_1 - X_1 Y_0}{J Y_1 - Y_0^2}, \quad (18)$$

$$C_{22}^n(R) = \frac{JX_1 - X_0Y_0}{JY_1 - Y_0^2}, \quad (19)$$

where

$$Y_p = \sum_{j=1}^J \omega_j^{2(p+1)}, \quad p = 0, 1.$$

The coefficients  $C_{ki}^n(R)$  allow to estimate the critical confinement parameter  $\omega_0$  for a given state as a function of the internuclear distance. Below the ionization threshold the energy of the confined molecule for each state is smaller than for the confined ion, i.e.

$$E_0^n(R) + C_{k1}^n(R)\omega^2 \dots + C_{kk}^n(R)\omega^{2k} < E_0^{0+}(R) + C_{k1}^{0+}(R)\omega^2 \dots + C_{kk}^{0+}(R)\omega^{2k}. \quad (20)$$

For  $k = 1$ , the critical confinement parameter for the  $n$ -th state for which the energy of an ion is equal to the energy of a neutral molecule is

$$\omega_0^n(1, R) = \sqrt{\frac{E_0^n(R) - E_0^{0+}(R)}{C_{11}^{0+}(R) - C_{11}^n(R)}}. \quad (21)$$

For  $k = 2$ , it can be shown that for the  $n$ -th state the inequality (20) is fulfilled for

$$\omega < \omega_0^n(2, R) = \sqrt{\frac{-b + \sqrt{b^2 - 4ac}}{2a}}, \quad (22)$$

where  $a = C_{22}^n(R) - C_{22}^{0+}(R)$ ,  $b = C_{21}^n(R) - C_{21}^{0+}(R)$ ,  $c = E_0^n(R) - E_0^{0+}(R)$ . It is worth to notice that the critical confinement parameter is a function of the internuclear distance.

## 4 Results and Discussion

The potential energy curves corresponding to the first two excited electronic states  $E_\omega^1(R)$  and  $E_\omega^2(R)$  are compared with the potential energy curve  $E_\omega^{0+}(R)$  of the ground state of the  $\text{HeH}^+$  ion in Fig. 1. The binding energies  $D_\omega^n$ ,  $n = 1, 2$  of these two states as functions of the strength of the confinement change in an irregular way. The first excited state becomes less stable with increasing  $\omega$ . In the unconfined case the binding energy is equal to  $D_{0,0}^1 = 92.98 \text{ mE}_h$ . In the case of the confined molecule with  $\omega = 0.1$  the binding energy is equal to  $D_{0,1}^1 = 77.71 \text{ mE}_h$  that is only 83.6% of  $D_{0,0}^1$ . In the confined molecule there appears an energy barrier of  $B_{0,1}^1 = 19.43 \text{ mE}_h$  and the dissociation may occur by tunneling. The opposite behaviour is observed in the second excited state. The confined molecule is more stable than the unconfined molecule. The binding energies in

this case are  $D_{0,1}^2 = 103.97 \text{ mE}_h$  and  $D_{0,0}^2 = 80.34 \text{ mE}_h$ , i.e.  $D_{0,1}^2$  constitutes 129.4% of  $D_{0,0}^1$ . Another important feature of the confined systems clearly seen in the Figure is the different behaviour of the neutral and ionized species. The shift of the potential energy curves in the ionized system is by an order of magnitude smaller than in the neutral system.

MRCI potential energy curves have been obtained for three values of  $\omega$  (for  $\omega = 0.0, 0.1, 0.2$ ). In order to investigate the  $\omega$ -dependence in more detail the intermediate energy values have been derived using an interpolation formula given by Eq. (12). The parameters in Eq. (16) for  $k = 1$  have been taken as  $\{J = 1, \omega_1 = 0.1\}$  and for  $k = 2$  as  $\{J = 2, \omega_1 = 0.1, \omega_2 = 0.2\}$ . As a consequence  $\tilde{E}_{0,1,1}^n(R) = E_{0,1}^n$ ,  $\tilde{E}_{0,1,2}^n(R) = E_{0,1}^n$ , and  $\tilde{E}_{0,2,2}^n(R) = E_{0,2}^n$ . Figure 2 illustrates the high quality of this approximation. The left part of the Figure presents the first-order approximation ( $k = 1$ ) to the ground state energy of  $\text{HeH}^+$  ( $E^{0+}$ ). The confinement parameter is small and equal to 0.05 and, in consequence, the quality of the approximation is very good. The difference between the exact energy and the interpolated values is of the order  $10^{-5} \text{ E}_h$ . In cylindrical confinement the ground state of  $\text{HeH}$  is unbound regardless of the strength of the confinement. The corresponding potential energy curves are shown in Fig. 2 (middle and right). As can be seen, the first-order interpolation gives correct results up to  $\omega = 0.2$  while the second-order interpolation is correct up to  $\omega = 0.4$ .

The confinement contributions to the potential energy curves of the  $\text{HeH}$  molecule, i.e. the differences

$$\delta E^n(\omega, R) = \tilde{E}_{\omega,2}^n(R) - E_0^n(R), \quad (23)$$

are shown in Fig. 3 for  $n = 1, 2, 3, 4$  (upper figures), where  $n = 1$  corresponds to the first excited state  $A^2\Sigma^+$ ,  $n = 2$  to the second  $B^2\Pi$ ,  $n = 3$  to the third  $C^2\Sigma^+$ , and  $n = 4$  to the fourth excited state  $D^2\Sigma^+$ . The differences are plotted for several values of  $\omega$ , starting with  $\omega = 0.01$  in steps of 0.02. The vertical lines denote the positions of the minima of the potential energy curves, i.e. the values of  $R_e$ . As one can see, in all the cases the confinement does not influence the bond length:  $R_e = 1.40 \text{ bohr}$  for  $n = 1, 2, 4$  and  $R_e = 1.60 \text{ bohr}$  for  $n = 3$ . This behaviour is different to that in the case of a confined  $\text{H}_2$  molecule where the confinement leads to a considerable reduction of the bond length [20]. An intuitive explanation of this difference is fairly simple: The cylindrical confinement moves the electronic charge closer to the molecular bond. In the ground state of a strongly bound molecule, like  $\text{H}_2$  or  $\text{H}_2^+$ , the electronic cloud is compact and its compression in the direction of the molecular axis results in an increase of the electronic density mainly in the area between the nuclei and, consequently, leads to a decrease of  $R_e$ . In a Rydberg molecule the Rydberg electron cloud is diffuse. Therefore, after the compression caused by confinement, a considerable amount of the electronic charge is moved to the area outside of the nuclei. Depending on the ratio of the charge shifted to the area outside and inside of the nuclei, the confinement may lead both to an increase or to a decrease of the bond length.

While the cylindrical confinement does not change the equilibrium distance, it does affect the shape of the potential energy curves. Only  $\delta E^2$  changes in a monotonic way with the internuclear distance. The energy barrier present in Fig. 1 is also seen in Fig. 3 (maxima of  $\delta E^1$ ). More complicated shapes of the potential energy curves appear in the higher excited states, as indicated by several extrema of  $\delta E^3$  and  $\delta E^4$ . The differences between the energies of the excited states ( $n = 1, 2, 3, 4$ ) of HeH and the energy of the ground state of HeH<sup>+</sup>, evaluated for several values of  $\omega$

$$\Delta E^n(\omega, R) = \tilde{E}_{\omega,2}^n(R) - E_{\omega}^{0+}(R) \quad (24)$$

are also presented in Fig. 3 (lower figures). Only the negative values of  $\Delta E^n$  for which the confinement parameter  $\omega$  is smaller than the critical one are displayed in Fig. 3. One can clearly see the ranges of  $\omega$  and of the internuclear distances  $R$  for which the  $n$ -th electronic state is bound.

The critical confinement parameters as function of  $R$  calculated for  $k = 1$  (Eq. (21)) and for  $k = 2$  (Eq. (22)) are presented in Fig. 4. As might be expected, the higher is the excitation the smaller are the critical confinement parameters. Furthermore, the larger are the  $\omega$  values, the more important are terms proportional to  $\omega^4$ , i.e. the contributions due to the second-order perturbation. However, it may be seen from Fig. 4 that the qualitative behaviour of  $\omega_0$  is, in all cases, correctly described by the first-order perturbation corrections. In the case of the two lowest excited states the critical values of  $\omega$  at  $R = R_e$  (the equilibrium distances are marked by  $\times$ ) evaluated using the first- and the second-order perturbation differ by  $\sim 20\%$  ( $n = 1$ ) and  $\sim 10\%$  ( $n = 2$ ). For the higher states ( $n = 3$  and  $n = 4$ ) already the first-order approximation gives accurate results.

The potential energy curves of HeH for the states with  $n = 1, 2, 3, 4$  are displayed in Fig. 5. The solid lines correspond to the limits of stability of the given state at the equilibrium distance. In each case the critical value of confinement parameter  $\omega_0^n(k, R)$  derived for  $k = 2$  and  $R = R_e$  is also given.

## 5 Final remarks

Rydberg molecules confined by a cylindrical harmonic potential behave differently than strongly bound diatomic molecules. In particular, in this case the confinement does not lead to any shortening of the bond lengths. The ionization by pressure is caused by rather weak confinements. In consequence, the physically interesting range of  $\omega$  extends from 0 to  $\sim 0.1$  and therefore the effects of confinement may be adequately described using perturbation theory. For the ground state, which is well separated from the excited states, and for small coefficients in the expansion (13), the perturbation theory gives also correct results for larger  $\omega$ .



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## Figure captions

Figure 1: Potential energy curves of the first excited state  $A^2\Sigma^+$  (left) and of the second excited state  $B^2\Pi$  (right), solid lines, of the HeH molecule and of the  $X^1\Sigma^+$  ground state (dashed lines) of the  $\text{HeH}^+$  ion for  $\omega = 0.0$  and  $\omega = 0.1$ .

Figure 2: Potential energy curve of the ground state  $X^1\Sigma^+$  of the confined  $\text{HeH}^+$  ion (solid line) and its approximation resulting from the linear interpolation ( $k = 1$ ) (crosses) for  $\omega = 0.05$  (left) and potential energy curves of the ground state  $X^2\Sigma^+$  of the confined HeH molecule (solid lines) and their approximations (crosses) resulting from the first-order (middle) and second-order (right) interpolations. The consecutive curves correspond to an increment of  $\omega$  equal to 0.1.

Figure 3: Differences  $\delta E^n(\omega, R)$ , Eq. (23), between the energies of the excited states ( $n = 1, 2, 3, 4$ ) of the confined HeH molecule and the energies of the same states of the free HeH molecule (upper figures) and differences  $\Delta E^n(\omega, R)$ , Eq. (24), between the energies of the excited states ( $n = 1, 2, 3, 4$ ) of the confined HeH molecule and the energy of the ground state  $X^1\Sigma^+$  of the  $\text{HeH}^+$  ion (lower figures). The consecutive curves correspond to an increment of  $\omega$  equal to 0.02.

Figure 4: Critical confinement parameters  $\omega_0^n(k, R)$  for the excited states of the HeH molecule:  $A^2\Sigma^+$  ( $n = 1$ ),  $B^2\Pi$  ( $n = 2$ ),  $C^2\Sigma^+$  ( $n = 3$ ),  $D^2\Sigma^+$  ( $n = 4$ ), as function of the internuclear distance  $R$  obtained by using linear (solid lines) and quadratic (broken lines) interpolation formulas.

Figure 5: Potential energy curves of the excited states  $A^2\Sigma^+$  ( $n = 1$ ),  $B^2\Pi$  ( $n = 2$ ),  $C^2\Sigma^+$  ( $n = 3$ ), and  $D^2\Sigma^+$  ( $n = 4$ ) of the confined HeH molecule for the critical confinement parameter  $\omega_0^n(2, R_e)$  (solid lines), potential energy curves of the same states of the unconfined HeH molecule (dotted lines), and potential energy curve of the ground state  $X^1\Sigma^+$  of the  $\text{HeH}^+$  ion for  $\omega_0^n(2, R_e)$  (dashed lines).

Fig. 1.

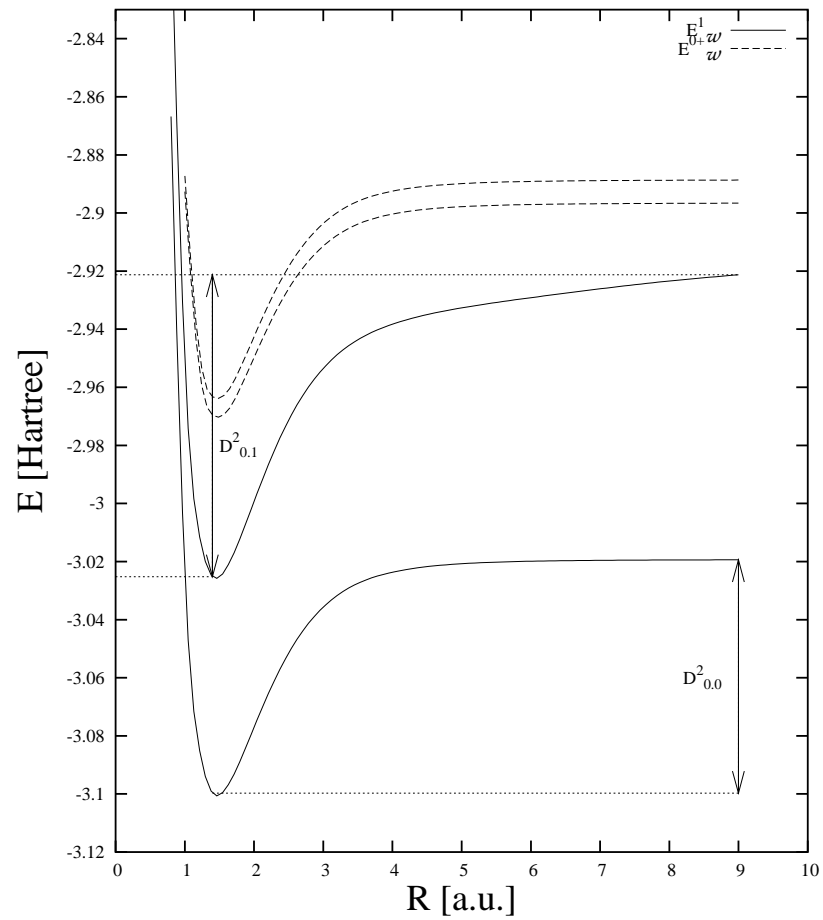
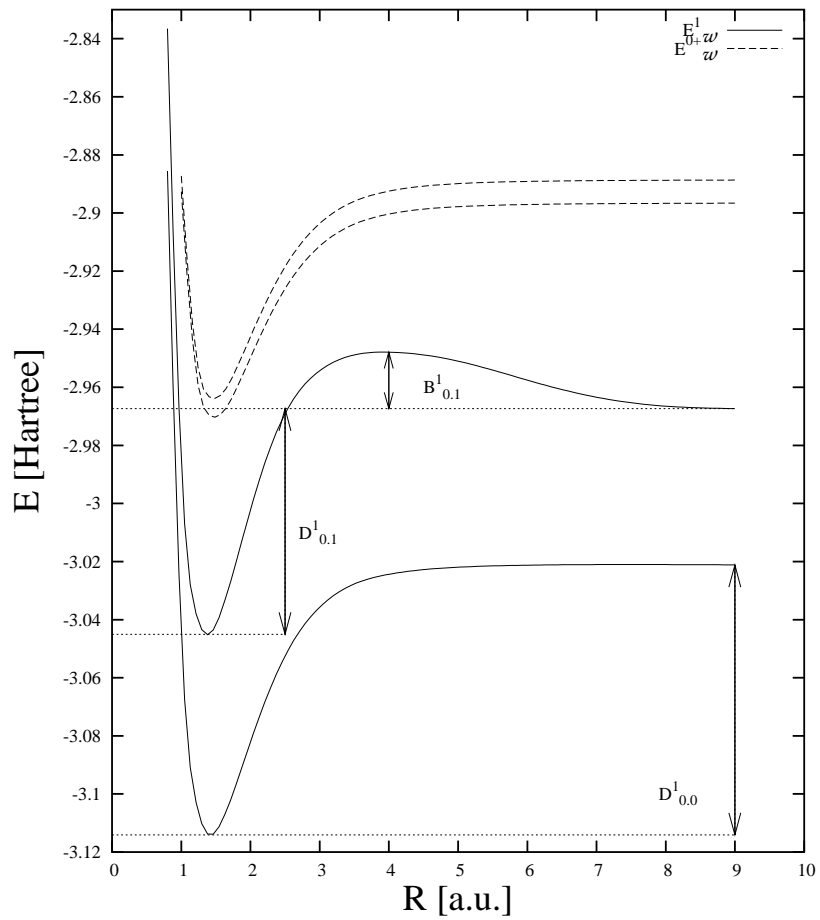
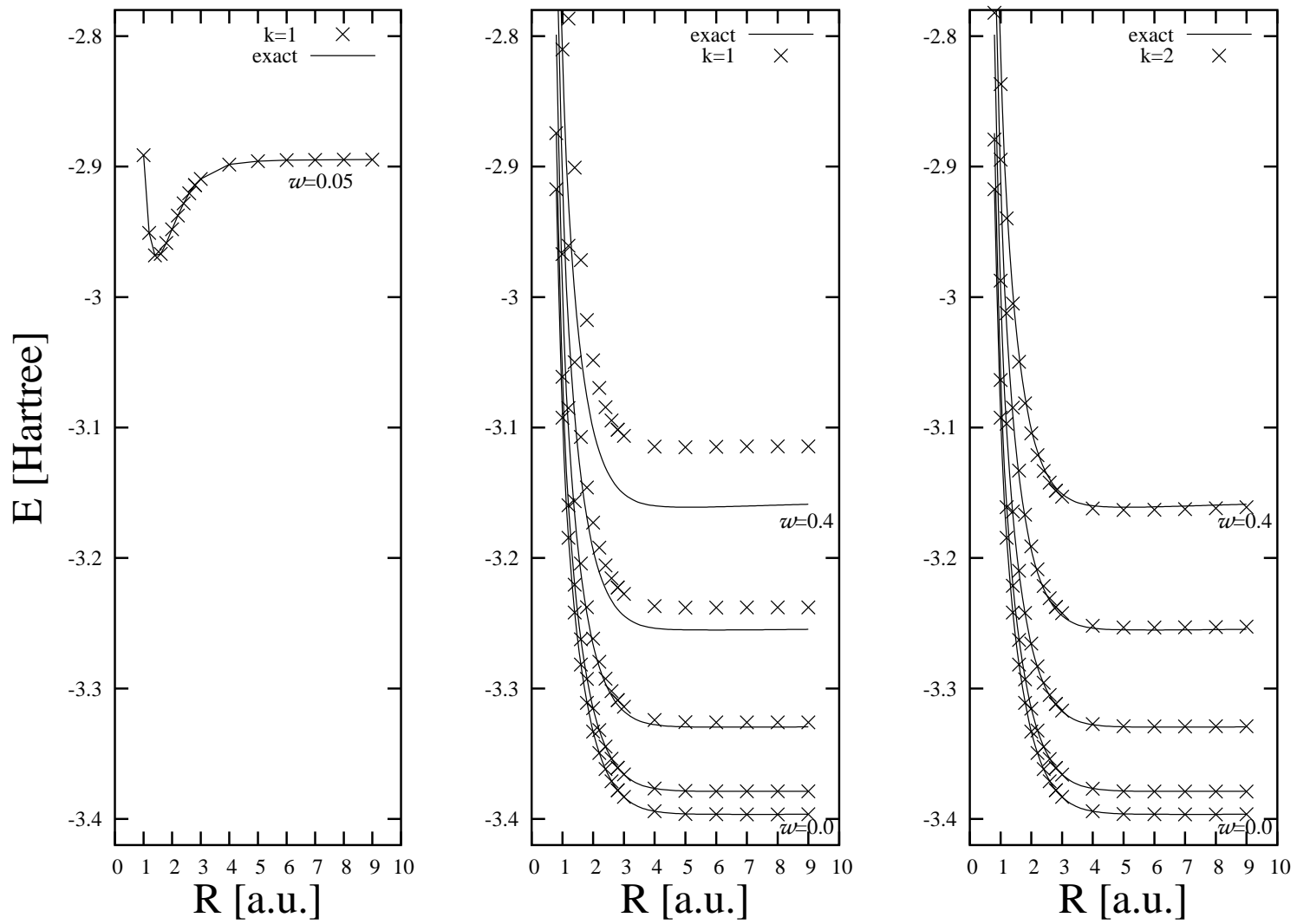


Fig. 2.



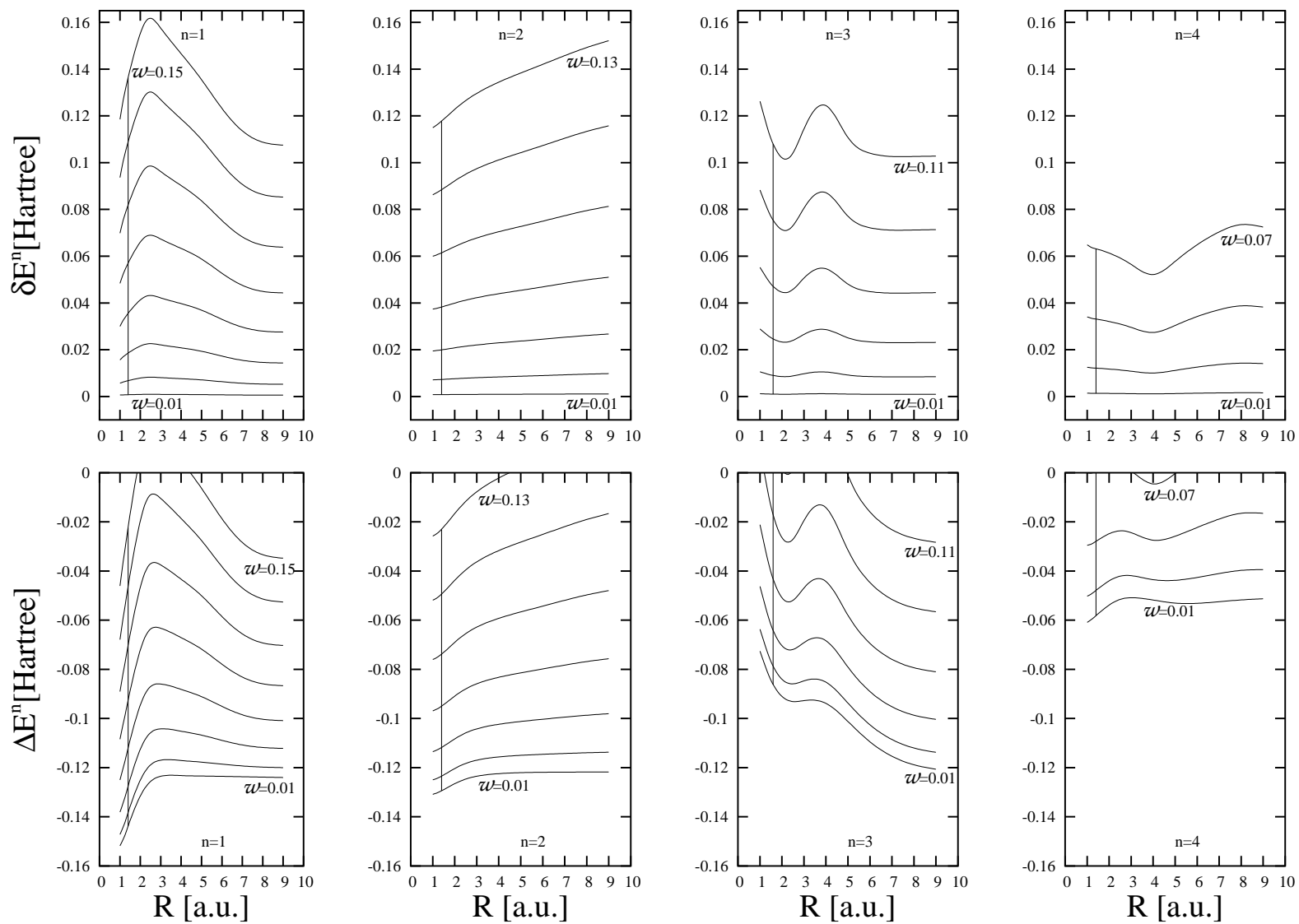


Fig. 3.

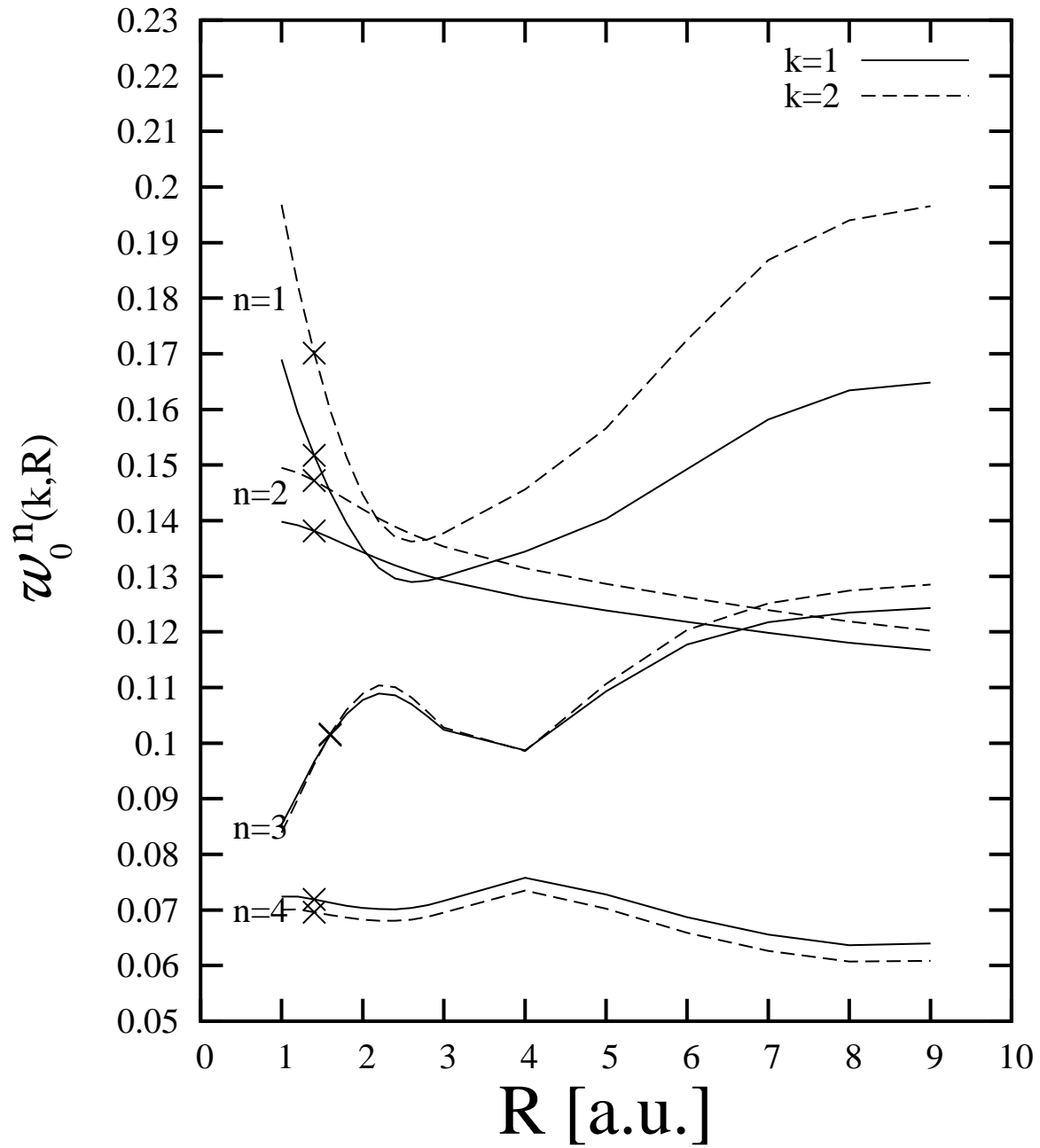


Fig. 4.

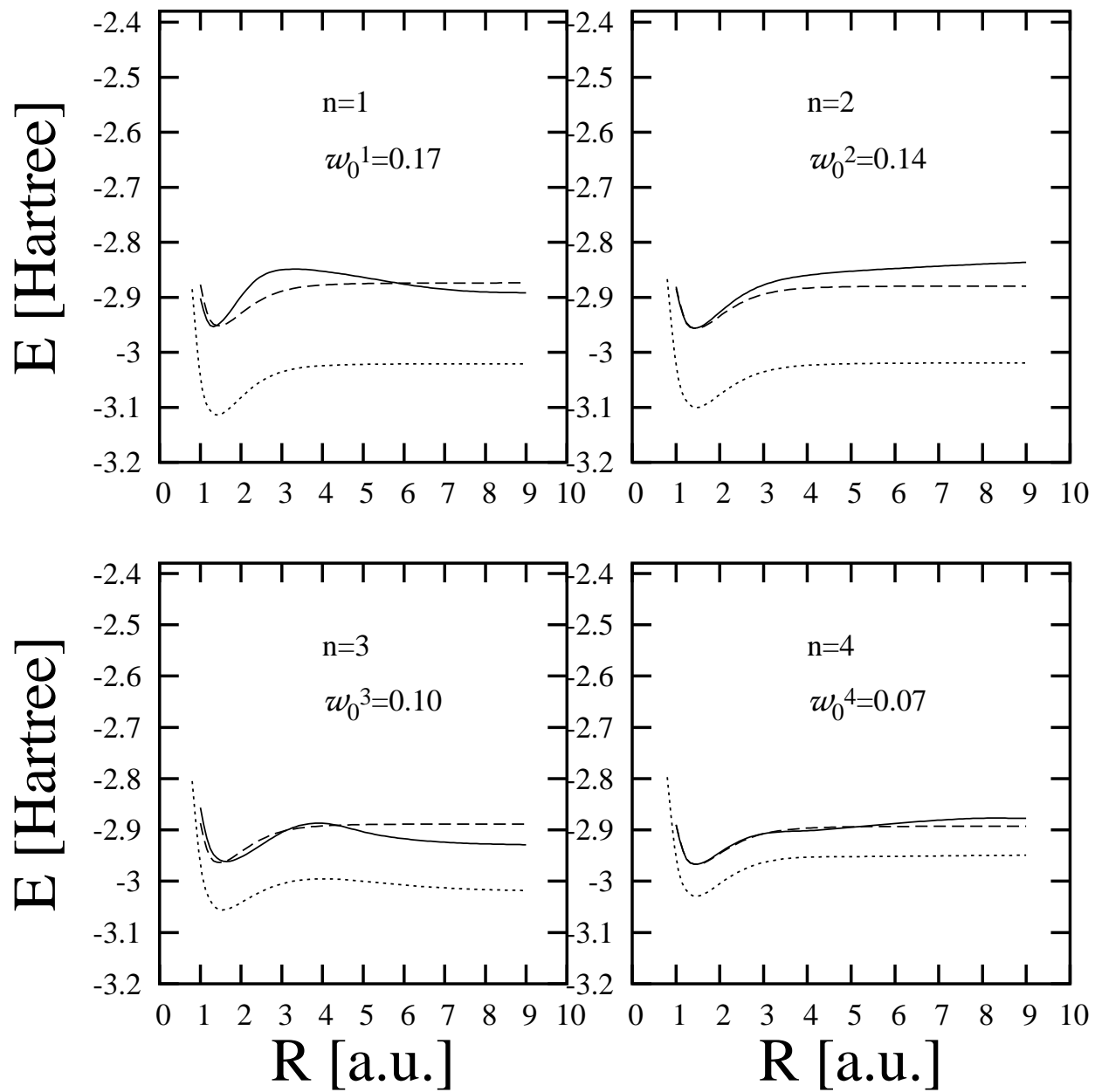


Fig. 5.