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## Theorems of the Hellman-Feynman type for stationary nonadiabatic systems

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Three theorems are proved for many-particle nonadiabatic systems, establishing the qualitative features of the dependence of the binding energy on the parameter which appears in the kinetic energy operator of the Hamiltonian. The first theorem establishes a relationship between the first and second derivatives of the binding energy with respect to this parameter. The second theorem imposes a restriction on the size of the first derivative. The third theorem determines upper and lower bounds of the system's binding energy for a given value of the parameter according to values of the binding energy associated with other values of the parameter. The theorems allow us to derive rigorous estimates of the binding energy and dissociation energy of nonadiabatic systems on the basis of data which exists for comparable systems. As an example, a lower bound is estimated for the dissociation energy of the muonium molecule.

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1. The Hellman-Feynman theorem,<sup>[1,2]</sup> establishing the dependence of the eigenvalue of a quantum mechanical system on a parameter in the Hamiltonian, has been widely used in calculations for molecular systems in the case when the Born-Oppenheimer adiabatic approximation is valid, and the parameter (usually the distance between nuclei) appears in the expression for the potential energy.<sup>[3-5]</sup> However, numerous cases exist when the parameter, for example, the ratio of the particle masses, appears in the kinetic energy operator and may be regarded as the parameter of nonadiabaticity. In this connection the conditions for applicability of the adiabatic approximation cannot be satisfied with regard to the selected subsystem. Cases also exist when one is not able to single out an adiabatic subsystem. Below we shall call both types of systems stationary nonadiabatic systems. In particular, examples of the indicated systems are given by: 1) electron-positron ions and molecules of the type  $e^-e^+e^{[6]}$ ; 2) systems of the type, atom (ion or molecule) + positron<sup>[7]</sup>; 3) muonic molecules of the type  $p\mu^-p^{[8,9]}$ ; 4) systems of the type, atom (ion or molecule) + muonium, for example,  $C_2H_4(\mu^+e^-)$ , or "muonium" water  $H(\mu^+e^-)O^{[9]}$ ; the broad class of systems formed out of quasiparticles (electrons and holes).<sup>[10]</sup>

Three general theorems of the Hellman-Feynman type are proved below for many-particle nonadiabatic systems. The following basic assumptions are utilized:

1) the particles interact according to a law of the type  $|r_{ij}|^{-n}$  and 2) the kinetic energy operator linearly depends on the parameter  $\alpha$ . The theorems determine the qualitative features of the dependence of a nonadiabatic system's binding energy  $B_0$  on the parameter  $\alpha$ . The first theorem establishes a relationship between the first and second derivatives of  $B_0$  with respect to  $\alpha$ . The second theorem imposes a limitation on the size of  $\partial B_0(\alpha)/\partial\alpha$ . The third theorem determines rigorous upper and lower bounds for  $B_0(\alpha)$  with respect to the values  $B_0(\alpha_1)$  and  $B_0(\alpha_2)$ , where  $\alpha_1 < \alpha < \alpha_2$ . The obtained results are qualitative in nature and, in analogy to other qualitative results in quantum mechanics,<sup>[11]</sup> they allow one to make relatively simple estimates.

2. Let the Schrödinger equation for an  $N$ -particle system have the form

$$H\Psi_k = -B_k\Psi_k, \quad (1)$$

where  $k$  denotes the totality of quantum numbers,  $k=0$  corresponds to the nondegenerate ground state of the system, and

$$H = T_1(r) + \alpha T_2(r) + V(r),$$

$$r = (r_1, r_2, \dots, r_N), \quad r_i = (x_i^1, x_i^2, x_i^3),$$

$$T_{1,2} = \sum_{ij, \mu\nu} b_{ij, \mu\nu}^{(1,2)} \frac{\partial^2}{\partial x_i^\mu \partial x_j^\nu},$$

$$\bar{T}_{1,2}(\alpha) = \langle 0 | T_{1,2} | 0 \rangle, \quad \bar{T}_{1,2}(\alpha) > 0;$$

$$\tau(\alpha) = \bar{T}_1(\alpha) / \bar{T}_2(\alpha), \quad (2)$$

$$V(rQ) = Q^{-n}V(r), \quad Q > 0, \quad n < 2. \quad (3)$$

The most general result for nonadiabatic systems is related to the use of the Hellman–Feynman theorem for Eq. (1):

$$\frac{\partial}{\partial \alpha} B_0(\alpha) = -\langle 0 | T_2 | 0 \rangle = -\bar{T}_2(\alpha). \quad (4)$$

It follows from this theorem that the system's binding energy monotonically decreases with increasing values of the parameter  $\alpha$ :

$$B_0(\alpha_1) > B_0(\alpha) > B_0(\alpha_2), \quad \alpha_1 < \alpha < \alpha_2. \quad (5)$$

The following theorems hold for Eq. (1):

**Theorem 1.** The inequality

$$-\frac{\partial^2}{\partial \alpha^2} [(\alpha+a)^{n/(2-n)} B_0(\alpha)] < 2(\alpha+a)^{-1} \frac{\partial}{\partial \alpha} [(\alpha+a)^{n/(2-n)} B_0(\alpha)]. \quad (6)$$

is satisfied for  $\alpha+a > 0$ ,  $a = \text{const}$ .

**Theorem 2.** The inequality

$$\frac{\partial}{\partial \alpha} [(\alpha+A)^{n/(2-n)} B_0(\alpha)] < 0. \quad (7)$$

is satisfied for  $\alpha < \alpha_2$  and  $A \geq \tau(\alpha_2)$ , where  $\tau$  is defined by Eq. (2).

**Theorem 3.** The following inequalities hold for given values  $B_0(\alpha_1)$  and  $B_0(\alpha_2)$  and fulfillment of the conditions  $\alpha_1 < \alpha < \alpha_2$ ,  $A > \tau(\alpha_2)$ :

$$\left(\frac{\alpha_1+A}{\alpha+A}\right)^{n/(2-n)} B_0(\alpha_1) > B_0(\alpha) > \left(\frac{\alpha_2+A}{\alpha+A}\right)^{n/(2-n)} B_0(\alpha_2). \quad (8)$$

**3.** The proof of Theorem 1 is based on the application of a special form of the scale transformation

$$r = (\alpha+a)^{1/(2-n)} \bar{r}, \quad (9)$$

taking into consideration the condition of homogeneity of the interparticle interaction potential (3), and generalizes the relationships used in a special case ( $n=1$ , four-particle system) for an analysis of nonadiabatic effects in molecules of the  $H_2$  type.<sup>[12-14]</sup> The transformation (9) reduces Eq. (1) to the form

$$H\bar{\Psi}_k = -\bar{E}_k \bar{\Psi}_k, \quad (10)$$

where

$$H = (\alpha+a)^{-1} [T_1(\bar{r}) + \alpha T_2(\bar{r})] + V(\bar{r}), \quad (11)$$

$$\bar{E}_k(\alpha, a) = (\alpha+a)^{n/(2-n)} E_k(\alpha), \quad (12)$$

and the equation<sup>1)</sup>

$$\frac{\partial^2}{\partial \alpha^2} H = -2(\alpha+a)^{-1} \frac{\partial}{\partial \alpha} H. \quad (13)$$

is satisfied. Introducing the notation  $\bar{K}_0 = \bar{H} + \bar{E}_0$  and differentiating Eq. (10), we obtain after transformations

$$\begin{aligned} \left\langle \bar{\Psi}_0 | \bar{K}_0 | \frac{\partial^2}{\partial \alpha^2} \bar{\Psi}_0 \right\rangle + 2 \left\langle \bar{\Psi}_0 | \frac{\partial}{\partial \alpha} \bar{K}_0 | \frac{\partial}{\partial \alpha} \bar{\Psi}_0 \right\rangle \\ + \left\langle \bar{\Psi}_0 | \frac{\partial^2}{\partial \alpha^2} \bar{K}_0 | \bar{\Psi}_0 \right\rangle = 0. \end{aligned} \quad (14)$$

The first term in (14) is equal to zero due to the hermitian property of the operator  $\bar{H}$ . By using Eq. (10) the second term in (14) can be written in the form

$$-2 \left\langle \frac{\partial}{\partial \alpha} \bar{\Psi}_0 | \bar{K}_0 | \frac{\partial}{\partial \alpha} \bar{\Psi}_0 \right\rangle.$$

Utilizing the Hellman–Feynman theorem (4) for Eq. (10) with respect to the parameter  $\alpha_1$ , the definition (12), and the relationship (13), Eq. (14) can be written in the form

$$\left[ \frac{\partial^2}{\partial \alpha^2} \bar{E}_0(\alpha, a) + 2(\alpha+a)^{-1} \frac{\partial}{\partial \alpha} \bar{E}_0(\alpha, a) \right] = 2 \left\langle \frac{\partial}{\partial \alpha} \bar{\Psi}_0 | \bar{K}_0 | \frac{\partial}{\partial \alpha} \bar{\Psi}_0 \right\rangle. \quad (15)$$

In order to estimate the sign of the matrix element in the right-hand side of Eq. (15) with the function  $\partial \bar{\Psi}_0 / \partial \alpha$  orthogonal to the ground state wave function  $\bar{\Psi}_0$  of Eq. (10), let us use the expansion

$$\frac{\partial}{\partial \alpha} \bar{\Psi}_0 = \sum_{k \geq 1} c_k \bar{\Psi}_k.$$

Upon utilization of the assumption concerning the orthogonality of the functions  $\bar{\Psi}_k$  for  $k \geq 1$ , this expansion allows us to write the right-hand side of Eq. (15) in the form

$$2 \sum_{k \geq 1} |c_k|^2 (\bar{E}_k - \bar{E}_0) > 0. \quad (16)$$

Taking account of inequality (16) and the definition (12), from (15) we obtain the relationship (6).

**4.** Let us consider the proof of Theorems 2 and 3. Let us find the solution of the equation

$$\left[ \frac{\partial}{\partial \alpha} \bar{E}_0(\alpha, A) \right]_{\alpha=\alpha_2} = 0. \quad (17)$$

Using the Hellman–Feynman theorem for Eq. (10) with respect to the parameter  $\alpha$ , we obtain  $\bar{A} = \tau(\alpha_2)$ . It follows from relationships (15)–(17) that the condition

$$\frac{\partial^2}{\partial \alpha^2} B_0(\alpha, \bar{A}) > 0.$$

is satisfied for  $\alpha_2 - \alpha \ll \alpha_2$ . Thus, the function  $\partial \bar{E}_0(\alpha, \bar{A}) / \partial \alpha$  is negative in a small neighborhood to the left of  $\alpha_2$  and increases with increasing values of  $\alpha$ . Repeating these arguments, we obtain the result that such a behavior of the function  $\partial \bar{E}_0(\alpha, \bar{A}) / \partial \alpha$  is characteristic for the entire region  $\alpha < \alpha_2$ . In this connection utilization of the condition  $A > \bar{A}$  only strengthens the inequality  $\partial \bar{E}_0 / \partial \alpha < 0$ . Taking the definition (12) into consideration, we obtain inequality (7).

For the proof of Theorem 3, we note that it follows from the differential properties of the functions  $\partial^2 \bar{E}_0 / \partial \alpha^2$  and  $\partial \bar{E}_0 / \partial \alpha$  that  $\bar{E}_0(\alpha, \bar{A})$  decreases with increasing values of  $\alpha$  for  $\alpha < \alpha_2$ . Taking this property and the definition (12) into consideration, we obtain the inequality

$$(\alpha' + \bar{A})^{n/(2-n)} B_0(\alpha') > (\alpha + \bar{A})^{n/(2-n)} B_0(\alpha). \quad (18)$$

for  $\alpha' < \alpha$ . Using the inequalities (5), we find that the

replacement of  $\bar{A}$  by  $A$  in inequality (18), where  $A > \bar{A}$ , strengthens this inequality. Taking this property into consideration, from (18) we obtain the inequalities (8). We note that the inequalities (8) are stronger than the rigorous estimate (5) which follows from the Hellman-Feynman theorem. Inequality (8) goes over into (5) for  $A \gg \alpha_2$ . One can also show that the lower bound in inequality (8) is closer to the exact value  $B_0(\alpha)$  than a linear extrapolation of this quantity with respect to the values  $B_0(\alpha_2)$  and  $(\partial B_0(\alpha)/\partial \alpha)_{\alpha=\alpha_2}$ .

5. Let us consider certain corollaries for the case of Coulomb systems ( $n=1$ ), a case of practical importance. These corollaries allow us, in particular, to obtain rigorous estimates of the binding energy and dissociation energy of nonadiabatic systems on the basis of data, which is obtained for comparable systems from calculations or experiment. The indicated data may pertain to the adiabatic domain. From Theorem 2, the virial theorem, and the Hellman-Feynman theorem for Eq. (1), it follows that the quantity  $\tau(\alpha)$ , characterizing the nonadiabaticity of the system according to the definition (2), is an increasing function of  $\alpha$ . On the other hand, it follows from the proof of Theorem 2 that, for  $A = \tau(\alpha_1)$  and  $\alpha_1 < \alpha$  inequality (7) goes over into the inequality

$$\partial/\partial \alpha (\alpha + \tau(\alpha)) > 0.$$

From this inequality follows the rigorous estimate

$$B_0(\alpha_1) \frac{\alpha_1 + \tau(\alpha_1)}{\alpha + \tau(\alpha_1)} < B_0(\alpha), \quad (19)$$

in which the quantities  $\alpha_1$ ,  $\tau(\alpha_1)$ , and  $B_0(\alpha_1)$  can refer to the adiabatic domain.

6. As an example let us estimate, with the aid of the inequality (19), the lower bound on the dissociation energy of a muonium molecule,  $(\mu^+e^-)_2 + D_\mu - (\mu^+e^-)_2$ . This example is of interest since the further development of accelerators will, in the near future, allow us to obtain a rather high flux of  $\mu$  mesons. As the initial ("adiabatic") data we shall use the parameters for the hydrogen molecule. In Eq. (1) for the case under consideration, we obtain in atomic units

$$T_1 = 1/2 (\nabla_{r_1}^2 + \nabla_{r_2}^2), \quad T_2 = 1/2 (\nabla_{u_1}^2 + \nabla_{u_2}^2), \\ \alpha_p \leq \alpha \leq \alpha_m, \quad \alpha_p = m_e/m_\mu,$$

where  $\alpha_\mu = m_e/m_\mu = 1/206.8$ .<sup>[9]</sup> The Born-Oppenheimer parameters are given by  $(\alpha_p)^{1/4} = 0.15$  and  $(\alpha_\mu)^{1/4} = 0.27$ , respectively. The quantity  $\tau(\alpha_1 = \alpha_p)$  in relation (19) can be estimated by using the following empirical dependence for the hydrogen molecule:

$$B_0(\alpha) = a - b\sqrt{\alpha}, \quad (20)$$

where  $a = 1.174$  and  $b = 0.382$  in atomic units.<sup>[12]</sup> Upon taking relations (2) and (20) into consideration, it fol-

lows from the virial theorem and from the Hellman-Feynman theorem that, in the hydrogen molecule the ratio of the electrons' kinetic energy to the kinetic energy of the nucleus amounts to

$$k(\alpha) = \frac{\alpha}{\tau(\alpha)} = \frac{b\sqrt{\alpha}}{2a - 3\sqrt{\alpha}}, \quad (21)$$

where for the molecules  $H_2$  and  $(\mu^+e^-)_2$  we accordingly have

$$k_H = k(\alpha = \alpha_p) = 4.0 \cdot 10^{-3} \text{ and } k_\mu = k(\alpha = \alpha_\mu) = 1.3 \cdot 10^{-2}.$$

Substituting the value  $\tau(\alpha_p)$  determined from Eq. (21) into relation (19), we obtain an estimate for the lower bound of the muonium molecule's dissociation energy  $D_\mu > D_{\min}$ , where

$$D_{\min} = (a - b\alpha_p^{1/2}) \left( 1 - \frac{\alpha_p - \alpha_p}{\alpha_\mu + 2a\alpha_p^{1/2}b^{-1} - 3\alpha_p} \right) - \frac{1}{1 + \alpha_\mu}.$$

$D_{\min} = 3.7$  eV for the values of the parameters indicated above. For comparison we note that, in agreement with relation (20)  $[D(H_2) - D_{\min}]/D(H_2) \approx \frac{1}{7}$ , extrapolation of relationship (20) to the value  $\alpha = \alpha_\mu$  gives  $D_\mu = 4.27$  eV.

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<sup>1</sup>Here and below the usual assumption is made concerning the existence of the corresponding derivatives.

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