

Corrections to the Born-Oppenheimer approximation by means of perturbation theory

Francisco M. Fernández*

Departamento de Química Física, Universidad de Extremadura, 06071 Badajoz, Spain

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We develop an efficient method for the calculation of corrections to the Born-Oppenheimer approximation by means of perturbation theory. The perturbation terms through sixth order in the small parameter $\kappa = (m/M)^{1/4}$, where m and M are, respectively, electronic and nuclear masses, allow the construction of an effective vibrational Hamiltonian that takes into account adiabatic and nonadiabatic effects. The latter is negative and linearly dependent on the vibrational quantum numbers. We illustrate the application of the main equations and verify the general results by means of an exactly solvable model of two coupled harmonic oscillators.

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I. INTRODUCTION

Recently Patterson [1] derived simple expressions for the energy corrections to the Born-Oppenheimer approximation valid to first order in the particle-to-oscillator mass ratio m/M . His results show that the diabatic (or nonadiabatic) energy corrections for H_2^+ are negative and depend linearly on the vibrational quantum number in agreement with previous variational calculations [2]. Many years ago Van Vleck [3] derived a similar expression for nonadiabatic effects in diatomic molecules and stressed its linear dependence on the vibrational quantum number. This nonadiabatic contribution is proportional to ω/M , where ω is the oscillator frequency [1,3]. Since $\omega \propto 1/\sqrt{M}$, such a term is actually of order $(m/M)^{3/2}$. The perturbation method proposed by Patterson [1] is not a pure expansion in m/M and therefore it is unsuitable for the estimation of the magnitude of each correction in terms of that mass ratio.

The main ideas for the separate treatment of electrons and nuclei in molecules and crystals are due to Born and Oppenheimer [4]. The method was lately revisited by Born and Huang [5] who worked out the separation through the application of perturbation theory to the stationary states of the actual system and also to the stationary states of an auxiliary model in which the nuclei remain clamped at a given configuration. Here the perturbation parameter is $\kappa = (m/M)^{1/4} \ll 1$, where m is the electronic mass and M is a typical nuclear mass. This perturbation approach clearly reveals the dependence of each term on the mass ratio m/M . Although straightforward, the method of Born and Huang [5] is lengthy and requires great ingenuity to figure out how to combine the two sets of perturbation equations to obtain the desired results. Therefore, it is unsuitable for the treatment of

larger orders.

It is our purpose to rewrite the perturbation method of Born and Huang [5] in a simpler and more convenient way. In Sec. II we develop the main equations of perturbation theory up to sixth order, two orders more than those considered by Born and Huang [5], for a system with many electrons and nuclei and compare our results with those obtained by Patterson [1] for the particular case of H_2^+ . In Sec. III we verify the general results and theoretical conclusions by means of a simple, exactly solvable, model. In Sec. IV we discuss the main results, compare them with those from other approaches, and outline the application of the approximation to other examples of physical interest.

II. METHOD

For concreteness we consider the model discussed by Born and Huang [5] that describes a set of nuclei with masses $\{M_i\}$ and coordinates $X = \{X_i\}$ and a set of electrons with mass m and coordinates $x = \{x_i\}$. In the particular case of two equal nuclei and one electron we obtain the model for H_2^+ considered by Patterson [1] that omits electronic terms arising from the separation of the coordinates of the center of mass. In the coordinate representation the Hamiltonian operator reads

$$H = T_E + T_N + V(x, X), \quad (1)$$

where

$$T_E = -\frac{\hbar^2}{2m} \sum_i \frac{\partial^2}{\partial x_i^2}, \quad T_N = -\sum_i \frac{\hbar^2}{2M_i} \frac{\partial^2}{\partial X_i^2}, \quad (2)$$

are, respectively, the electron and nuclear kinetic-energy operators and $V(x, X)$ is the classical interaction potential. Following Born and Huang we neglect the translational and rotational motions of the system as a whole, an assumption which is certainly valid for solids [5]. In the case of molecules, on the other hand, the separation of the coordinates of the center of mass leaves kinetic-energy operators that differ from those in Eq. (2). However, one can easily adapt the method developed below to

*Permanent address: QUINOR, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Calle 47 y 115, Casilla de Correo 962, 1900 La Plata, Argentina.

treat such problems as well.

It is our purpose to solve approximately the Schrödinger equation for the stationary states of the system

$$H\Psi(x, X) = E\Psi(x, X) \quad (3)$$

by means of perturbation theory based on the fact that $M_i \gg m$. To this end we take into account the quantum-mechanical equation for the stationary states of a system of electrons moving around the nuclei clamped at a given configuration X :

$$H_E \Phi(x, X) = U(X)\Phi(x, X), \quad H_E = T_E + V(x, X). \quad (4)$$

For simplicity we restrict ourselves to a nondegenerate electronic state and without loss of generality we assume that Φ is real and normalized to unity:

$$\langle \Phi | \Phi \rangle_x = \int \Phi(x, X)^2 dx = 1. \quad (5)$$

From now on we use the subscripts x and X in the bracket notation to indicate integration over electronic and nuclear coordinates, respectively.

We define the nuclear and nonadiabatic functions

$$f(X) = \langle \Phi | \Psi \rangle_x, \quad (6)$$

$$F(x, X) = \Psi(x, X) - f(X)\Phi(x, X), \quad (7)$$

respectively. The latter is orthogonal to $\Phi(x, X)$ with respect to the electronic coordinates

$$\langle \Phi | F \rangle_x = 0 \quad (8)$$

and therefore takes into account nonadiabatic effects. One can also view $F(x, X)$ as a measure of the coupling of electronic and nuclear motions. It satisfies the differential equation

$$(H - E)F = -\Phi(T_N + U - E)f + [\Phi, T_N]f, \quad (9)$$

obtained by application of $H - E$ to both sides of (7) and use of (3) and (4). In this equation $[\Phi, T_N]$ denotes the commutator $\Phi T_N - T_N \Phi$. Taking into account (8) and choosing Ψ to be real it is not difficult to prove that

$$\langle \Psi | \Psi \rangle_x = \langle F | F \rangle_x + f(X)^2, \quad (10a)$$

$$\langle \Psi | \Psi \rangle_{x, X} = \langle F | F \rangle_{x, X} + \langle f | f \rangle_x. \quad (10b)$$

Applying $\langle \Phi |$ from the left of (9) we have

$$(T_N + U - E)f + \langle \Phi | [T_N, \Phi] \rangle_x f = -R(X), \quad (11)$$

where

$$\begin{aligned} R(X) &= \langle \Phi | T_N | F \rangle_x \\ &= \sum_i \frac{\hbar^2}{2M_i} \left[\left\langle \frac{\partial^2 \Phi}{\partial X_i^2} \middle| F \right\rangle_x + 2 \left\langle \frac{\partial \Phi}{\partial X_i} \middle| \frac{\partial F}{\partial X_i} \right\rangle_x \right]. \end{aligned} \quad (12)$$

To prove the second equality in Eq. (12) simply differentiate (8) twice with respect to the nuclear coordinates. Expanding the commutator $[T_N, \Phi]$ and taking into account the result of differentiating (5) once and twice with respect to the nuclear coordinates we obtain the adiabatic potential

$$W(X) = \langle \Phi | [T_N, \Phi] \rangle_x = \sum_i \frac{\hbar^2}{2M_i} \left\langle \frac{\partial \Phi}{\partial X_i} \middle| \frac{\partial \Phi}{\partial X_i} \right\rangle_x \geq 0. \quad (13)$$

Therefore, Eq. (11) becomes

$$[T_N + U(X) + W(X) - E]f(X) = -R(X). \quad (14)$$

If the terms $W(X)$ and $R(X)$, which couple electronic and nuclear motions, were negligible then the solutions to Eq. (14) would not differ greatly from the solutions to the related homogeneous equation

$$[T_N + U(X) - \mathcal{E}]g(X) = 0 \quad (15)$$

that give the Born-Oppenheimer energy \mathcal{E} . As shown below Eqs. (9) and (14) remarkably facilitate the application of perturbation theory

In order to introduce an appropriate perturbation parameter κ we consider scaled nuclear displacements $u = \{u_i\}$ from a given configuration $X_0 = \{X_{0i}\}$ according to $X_i = X_{0i} + \kappa u_i$. Because $\partial^2 / \partial X_i^2 = \kappa^{-2} \partial^2 / \partial u_i^2$ the nuclear kinetic-energy operator contains fractions $1/(M_i \kappa^2)$ that we rewrite $M \kappa^2 / (m M_i)$ through the choice $\kappa = (m/M)^{1/4}$. Here M is a representative nuclear mass; it may be just one particular mass from the set $\{M_i\}$, a reduced or effective nuclear mass or any other such choice that satisfies $m/M \ll 1$ and $M/M_i \simeq 1$. The former condition assures us that κ is a small parameter for perturbation theory. The nuclear kinetic-energy operator is of second order in κ :

$$T_N = \kappa^2 \tilde{T}_N, \quad \tilde{T}_N = -\frac{\hbar^2}{2m} \sum_i \frac{M}{M_i} \frac{\partial^2}{u_i^2}. \quad (16)$$

We next expand all the relevant quantities in power series of κ as follows:

$$G = \sum_{j=0}^{\infty} G^{(j)} \kappa^j, \quad G^{(j)} = \frac{1}{j!} \frac{\partial^j G}{\partial \kappa^j} \quad (\kappa=0). \quad (17)$$

If G depends on κ only through X as it is the case of H_E , $\Phi(x, X)$ and $U(X)$ then

$$\frac{\partial G}{\partial \kappa} = \sum_i \frac{\partial G}{\partial X_i} u_i. \quad (18)$$

Repeated application of this process shows that $G^{(j)}$ is a polynomial of u with only terms of order j ; this is to say, $G^{(1)}$ is linear, $G^{(2)}$ is quadratic, etc.

We now show how the present method facilitates the application of the perturbation theory of Born and Huang [5]. The two derivatives with respect to X in the function W defined by (13) give rise to a factor κ^2 when we change variables from X to u . Therefore, the first nonvanishing term in the expansion of W is at least of second order. The coefficients of κ^2 and κ^3 vanish because they contain $\partial \Phi^{(0)} / \partial u_i$ inside the bracket and $\Phi^{(0)}$ is independent of u . We conclude that W is at least of order κ^4 . The same argument shows that R is at least of order κ^3 from which it follows that $(T_N + U - E)f$ is at

least of this order [cf. Eq. (14)]. By simple inspection of the right-hand side of Eq. (9) one realizes that it is at least of order κ^3 and taking into account Eq. (8) one convinces oneself that F has to be at least of order κ^3 . Furthermore, looking at the expressions inside the brackets in Eq. (12) and remembering that $\Phi^{(0)}$ is independent of u and that $\Phi^{(1)}$ is linear in u one concludes that $R^{(j)}=0$ if $j < 6$. It follows from the results just obtained and Eq. (14) that the Born-Oppenheimer approximation is valid to order κ^4 ,

$$[T_N + U(X) - E]f(X) = O(\kappa^4), \quad (19)$$

and that the adiabatic approximation is valid to order κ^6 .

$$[T_N + U(X) + W(X) - E]f(X) = O(\kappa^6). \quad (20)$$

For instance, the latter tells us that the quantum-mechanical equation for the stationary states of the nuclei moving in the adiabatic potential $U(X) + W(X)$ yields the energy of the actual physical system with an accuracy of order κ^6 . The algebraic manipulation required to draw this conclusion by means of the original approach of Born and Huang [5] is quite tedious and involved. It is worth noticing that according to (10a) and the argument just given $f(X)^2$ gives the probability distribution for the nuclear positions with an error of order κ^6 coming from the first nonvanishing term of $\langle F|F \rangle_x$.

We next concentrate on the application of perturbation theory to Eq. (14) to obtain formal expressions for the calculation of corrections to the energy and stationary states. According to Eq. (10) if Ψ is normalized to unity then f will also be normalized to unity up to terms of order κ^6 . It follows from the perturbation equation of order zero $[U^{(0)} - E^{(0)}]f^{(0)} = 0$ that $E^{(0)}$ is just the electronic energy at the chosen, though yet undetermined, nuclear configuration

$$E^{(0)} = U^{(0)} = U(X_0). \quad (21)$$

The equation of first order reads $[U^{(1)} - E^{(1)}]f^{(0)} = 0$. Since $E^{(1)}$ is constant and $U^{(1)}$ is linear in u we conclude that both quantities have to vanish. The consistency condition $U^{(1)} = 0$ requires X_0 to be a nuclear configuration at a stationary point on the hypersurface $U(X)$:

$$\frac{\partial U}{\partial X_i}(X = X_0) = 0. \quad (22)$$

The perturbation equation of second order

$$[\tilde{T}_N + U^{(2)} - E^{(2)}]f^{(0)} = 0 \quad (23)$$

describes the motion of the nuclei under a quadratic potential energy function $U^{(2)}$. We have bound states if and only if this function is positive definite in which case X_0 is the nuclear configuration at equilibrium, that is to say, a minimum of $U(X)$. If n and ν denote the sets of electronic and vibrational quantum numbers, respectively, then up to second order in κ we have $E_{n\nu} = U_n(X_0) + \kappa^2 E_{n\nu}^{(2)}$ so that $|E_{n\nu} - E_{n'\nu'}| \gg |E_{n\nu} - E_{n\nu'}| = O(\kappa^2)$. The vibrational potential $U^{(2)}$ has inversion symmetry (i.e., with respect to the change $u \rightarrow -u$) and the solutions to (23) belong to pure g or

pure u representations [6]. The expressions of perturbation theory for Eqs. (14) and (15) are identical up to second order; therefore $\mathcal{E}^{(0)} = E^{(0)}$, $\mathcal{E}^{(1)} = 0$, $\mathcal{E}^{(2)} = E^{(2)}$, and $g^{(0)} = f^{(0)}$.

The equation of third order for the nuclear motion

$$[\tilde{T}_N + U^{(2)} - E^{(2)}]f^{(1)} + [U^{(3)} - E^{(3)}]f^{(0)} = 0 \quad (24)$$

is equivalent to the equation of first order for a harmonic oscillator perturbed by a cubic potential $U^{(3)}$. In the general case one expects some of the stationary states of the harmonic oscillator to be degenerate. Since the matrix elements of $U^{(3)}$ between degenerate harmonic-oscillator eigenfunctions vanish because of symmetry ($U^{(3)}$ changes sign under inversion) then $E^{(3)} = 0$ for all the states and degeneracy does not break at this order. Multiplication of Eq. (24) by $f^{(0)}$ followed by inversion shows that $f^{(0)}f^{(1)}$ belongs to a pure u representation and therefore $f^{(1)}$ is orthogonal to $f^{(0)}$ (in agreement with the earlier statement that f is normalized up to terms of order κ^6). The perturbation equation of third order for the function $g(X)$ is identical to (24) so that $\mathcal{E}^{(3)} = 0$ and $g^{(1)} = f^{(1)}$.

Before proceeding with the perturbation treatment of Eq. (14) we mention that the derivation of the formal expressions of perturbation theory for Eq. (4) is straightforward. Solving the perturbation equations

$$[H_E^{(0)} - U^{(0)}]\Phi^{(j)} = \sum_{k=1}^j [U^{(k)} - V^{(k)}]\Phi^{(j-k)}, \quad j=0,1,\dots \quad (25)$$

hierarchically, with $H_E^{(0)} = T_E + V(x, X_0)$, one obtains all the necessary coefficients $\Phi^{(j)}$ for the expansion of the stationary electronic states in powers of κ . This calculation is far from trivial for realistic models. Fortunately, just formal solutions suffice for the present discussion.

The perturbation equation of fourth order for the nuclei

$$[\tilde{T}_N + U^{(2)} - E^{(2)}]f^{(2)} + U^{(3)}f^{(1)} + [U^{(4)} + W^{(4)} - E^{(4)}]f^{(0)} = 0, \quad (26)$$

where

$$W^{(4)} = \sum_i \frac{\hbar^2 M}{2mM_i} \left\langle \frac{\partial \Phi^{(1)}}{\partial u_i} \left| \frac{\partial \Phi^{(1)}}{\partial u_i} \right\rangle_x = \text{const} > 0 \quad (27)$$

is identical to the equation of second order for a harmonic oscillator perturbed by cubic and quartic anharmonic potentials. The adiabatic effects amount to an additive constant. By simple inspection of the symmetry of the terms in Eq. (26) one expects degeneracy to be partially or totally broken at this order. Arguing as before one easily proves that $f^{(2)}$ and $f^{(0)}$ behave in the same way with respect to inversion. Comparing (26) with the equation of fourth order for (15),

$$[\tilde{T}_N + U^{(2)} - E^{(2)}]g^{(2)} + U^{(3)}g^{(1)} + [U^{(4)} - \mathcal{E}^{(4)}]g^{(0)} = 0, \quad (28)$$

and taking into account that $f^{(j)} = g^{(j)}$ for $j < 2$ we conclude that

$$E^{(4)} = \mathcal{E}^{(4)} + \mathcal{W}^{(4)} > \mathcal{E}^{(4)} \quad (29)$$

and $f^{(2)} = g^{(2)}$. The adiabatic energy is larger than the Born-Oppenheimer energy \mathcal{E} because $\mathcal{W}(X)$ is positive for all nuclear configurations and this fact is reflected in Eq. (29).

The equation of fifth order reads

$$\begin{aligned} & [\tilde{T}_N + U^{(2)} - E^{(2)}]f^{(3)} + U^{(3)}f^{(2)} \\ & + [U^{(4)} + \mathcal{W}^{(4)} - E^{(4)}]f^{(1)} \\ & + [U^{(5)} + \mathcal{W}^{(5)} - E^{(5)}]f^{(0)} = 0, \quad (30) \end{aligned}$$

where

$$\mathcal{W}^{(5)} = \sum_i \frac{3\hbar^2 M}{mM_i} \left\langle \frac{\partial \Phi^{(1)}}{\partial u_i} \left| \frac{\partial \Phi^{(2)}}{\partial u_i} \right\rangle_x \quad (31)$$

is linear in the coordinates u . This equation is equivalent to the expression of third order for a harmonic oscillator perturbed by linear, cubic, quartic, and quintic potentials. Comparing (30) with the corresponding equation for $g(X)$

$$\begin{aligned} & [\tilde{T}_N + U^{(2)} - E^{(2)}]g^{(3)} + U^{(3)}f^{(2)} \\ & + [U^{(4)} + \mathcal{W}^{(4)} - E^{(4)}]f^{(1)} + [U^{(5)} - E^{(5)}]f^{(0)} = 0, \quad (32) \end{aligned}$$

we conclude that $g^{(3)}$ is different from $f^{(3)}$.

The first nonadiabatic correction appears at sixth order,

$$\begin{aligned} & [\tilde{T}_N + U^{(2)} - E^{(2)}]f^{(4)} + U^{(3)}f^{(3)} \\ & + [U^{(4)} + \mathcal{W}^{(4)} - E^{(4)}]f^{(2)} + [U^{(5)} + \mathcal{W}^{(5)} - E^{(5)}]f^{(1)} \\ & + [U^{(6)} + \mathcal{W}^{(6)} - E^{(6)}]f^{(0)} = -R^{(6)}, \quad (33) \end{aligned}$$

where

$$\begin{aligned} \mathcal{W}^{(6)} &= \sum_i \frac{\hbar^2 M}{mM_i} \left[8 \left\langle \frac{\partial \Phi^{(1)}}{\partial u_i} \left| \frac{\partial \Phi^{(3)}}{\partial u_i} \right\rangle_x \right. \\ &\quad \left. + 6 \left\langle \frac{\partial \Phi^{(2)}}{\partial u_i} \left| \frac{\partial \Phi^{(2)}}{\partial u_i} \right\rangle_x \right], \\ R^{(6)} &= \sum_i \frac{\hbar^2 M}{mM_i} \left\langle \frac{\partial \Phi^{(1)}}{\partial u_i} \left| \frac{\partial F^{(3)}}{\partial u_i} \right\rangle_x. \quad (34) \end{aligned}$$

The new adiabatic contribution $\mathcal{W}^{(6)}$ is quadratic in u . In order to calculate the nonadiabatic term we need $F^{(3)}$ that is a solution to

$$\begin{aligned} [H^{(0)} - E^{(0)}]F^{(3)} &= [H_E^{(0)} - U^{(0)}]F^{(3)} \\ &= \sum_i \frac{\hbar^2 M}{mM_i} \frac{\partial \Phi^{(1)}}{\partial u_i} \frac{\partial f^{(0)}}{\partial u_i}. \quad (35) \end{aligned}$$

With the aid of the projection operator $P = \hat{1} - |\Phi^{(0)}\rangle_{xx} \langle \Phi^{(0)}|$, $\hat{1}$ being the identity operator, we write $F^{(3)}$ as

$$F^{(3)} = \sum_i \frac{\hbar^2 M}{mM_i} [H_E^{(0)} - U^{(0)}]^{-1} P \frac{\partial \Phi^{(1)}}{\partial u_i} \frac{\partial f^{(0)}}{\partial u_i}. \quad (36)$$

Substituting (36) into (34) we have

$$R^{(6)} = \sum_i \sum_j \frac{\hbar^4 M^2}{m^2 M_i M_j} K_{ij} \frac{\partial^2 f^{(0)}}{\partial u_i \partial u_j}, \quad (37)$$

where

$$K_{ij} = \left\langle \frac{\partial \Phi^{(1)}}{\partial u_i} \left| [H_E^{(0)} - U^{(0)}]^{-1} P \left| \frac{\partial \Phi^{(1)}}{\partial u_j} \right\rangle_x. \quad (38) \right.$$

Equation (37) shows that we can incorporate the nonadiabatic effects of order κ^6 in our calculation by means of the kinetic-energy operator

$$\mathcal{T} = - \sum_i \sum_j \frac{\hbar^4 M^2 K_{ij}}{m^2 M_i M_j} \frac{\partial^2}{\partial u_i \partial u_j}. \quad (39)$$

In fact, the eigenfunctions of the effective vibrational Hamiltonian,

$$\begin{aligned} H_{\text{vib}} &= \tilde{T}_N - \kappa^4 \mathcal{T} + U^{(2)} + \kappa U^{(3)} + \kappa^2 [U^{(4)} + \mathcal{W}^{(4)}] \\ &+ \kappa^3 [U^{(5)} + \mathcal{W}^{(5)}] + \kappa^4 [U^{(6)} + \mathcal{W}^{(6)}], \quad (40) \end{aligned}$$

satisfy all the perturbation equations shown above. If we write

$$H_{\text{vib}} f_{nv} = \epsilon_{nv} f_{nv}, \quad (41)$$

where H_{vib} depends on the electronic quantum numbers n through Φ , then the energies of the stationary states of the system up to sixth order are

$$E_{nv} = U_n^{(0)} + \kappa^2 \epsilon_{nv} + \mathcal{O}(\kappa^7). \quad (42)$$

To obtain more explicit expressions for the coefficients K_{ij} we have to solve the perturbation equation of first order for the electronic states

$$[H_E^{(0)} - U^{(0)}]\Phi^{(1)} = -V^{(1)}\Phi^{(0)}. \quad (43)$$

Making use again of the projection operator P we have

$$\Phi^{(1)} = [U^{(0)} - H_E^{(0)}]^{-1} P V^{(1)} \Phi^{(0)} \quad (44)$$

and Eq. (38) becomes

$$K_{ij} = \langle \Phi^{(0)} | \frac{\partial V^{(1)}}{\partial u_i} [H_E^{(0)} - U^{(0)}]^{-3} P \frac{\partial V^{(1)}}{\partial u_j} | \Phi^{(0)} \rangle_x \quad (45)$$

because P commutes with any function of $H_E^{(0)}$ and $P^2 = P$.

In the following discussion we assume that $U^{(0)}$ is the ground-state electronic energy. If we insert P to the left of $[H_E^{(0)} - U^{(0)}]^{-3}$ in Eq. (45) we obtain a more symmetric expression showing that the diagonal elements K_{ii} are positive. Moreover, since the quadratic form obtained by summation of $K_{ij} u_i u_j$ over all nuclear coordinates is positive definite then all the eigenvalues of the matrix (K_{ij}) are positive. As a result the expectation value of \mathcal{T} is positive and thus the nonadiabatic contribution to the vibrational energy is negative. Writing the nonadiabatic kinetic-energy operator \mathcal{T} in terms of normal coordinates [5] and taking into account the properties of the eigenfunctions of the harmonic oscillator one easily proves that the nonadiabatic contribution of order κ^6 is linear

with respect to the vibrational quantum numbers. Therefore, if E^A denotes the adiabatic energy then up to sixth order of perturbation theory $E^A - E$ is positive and increases linearly with the vibrational quantum numbers. We have thus generalized Patterson's result [1] to the multidimensional case.

It is easy to prove that the Born-Oppenheimer and adiabatic energies bracket the exact energy of the system: $\mathcal{E} < E < E^A$ [7]. (Notice that Brattsev's notation [7] is different from ours as he calls adiabatic and variational what we have termed Born-Oppenheimer and adiabatic energies, respectively.) The values of \mathcal{E} and E^A given by Beckel, Hansen, and Peek [8] and the nonadiabatic results obtained by Kohl and Shipsey [2] provide, for the particular case of H_2^+ , an example of the two inequalities just mentioned.

The perturbation coefficients for the stationary states of the system are of the form

$$\begin{aligned}\Psi^{(j)} &= \sum_{k=0}^j f^{(k)} \Phi^{(k-j)}, \quad j < 3, \\ \Psi^{(j)} &= \sum_{k=0}^j f^{(k)} \Phi^{(k-j)} + F^{(j)}, \quad j \geq 3.\end{aligned}\quad (46)$$

Our expressions through fourth order agree with those obtained by Born and Huang [5]. We have extended the calculation to sixth order to show the occurrence of nonadiabatic effects. The derivation of perturbation corrections of larger order is straightforward following the lines already indicated above.

In order to compare our general results with those obtained by Patterson [1] for the particular case of H_2^+ we specialize in one nuclear degree of freedom. Denoting $H(\kappa, x, u)$ the Hamiltonian operator after the change of nuclear variables one easily verifies that $H(-\kappa, x, u) = H(\kappa, x, -u)$. Since the state is nondegenerate $E(-\kappa) = E(\kappa)$ and all the energy perturbation corrections of odd order vanish.

Taking into account a complete set of electronic states $\{\Phi_n^{(0)}, n=0, 1, \dots\}$ at the equilibrium configuration of the lowest one the only constant $K_{11} = K$ is

$$K = \sum_{n>0} \frac{|\langle \Phi_n^{(0)} | \frac{\partial V^{(1)}}{\partial u} | \Phi_0^{(0)} \rangle|^2}{[U_n^{(0)} - U_0^{(0)}]^3}.\quad (47)$$

As argued before for the general case $K > 0$ because $U_n^{(0)} - U_0^{(0)} > 0$. For this particular case we have

$$\begin{aligned}E^A - E &= -\kappa^6 \frac{\hbar^4 K}{m^2} \langle f^{(0)} | \frac{\partial^2}{\partial u^2} | f^{(0)} \rangle_u + O(\kappa^7) \\ &= \kappa^6 \frac{\hbar^2 K}{2m} \omega(v + \frac{1}{2}) + O(\kappa^7),\end{aligned}\quad (48)$$

where $v=0, 1, \dots$ is the vibrational quantum number, $\omega = \sqrt{k/m}$, and k is the harmonic oscillator force constant. Notice that it is the electronic mass that appears in our definition of ω ; we recover the ordinary oscillator frequency as $\kappa^2 \omega = \sqrt{k/M}$. Equation (48) shows that $E^A - E$ increases linearly with the vibrational quantum number in agreement with variational calculations [2].

Patterson [1] drew the same conclusion by means of a different argument. Our results clearly show that such nonadiabatic effects are of order $\kappa^6 = (m/M)^{3/2}$ as argued in the Introduction.

In closing we consider the expansion of the state of the system in a basis set of electronic functions Φ_n solutions to

$$[H_E - U_n(X)]\Phi_n(x, X) = 0.\quad (49)$$

Substitution of

$$\Psi(x, X) = \sum_m f_m(X) \Phi_m(x, X)\quad (50)$$

into Eq. (3) yields a set of coupled equations for the coefficients $f_m(X)$ [5],

$$(T_N + U_n + W_n - E)f_n = \sum_{m \neq n} \langle \Phi_n | [\Phi_m, T_N] \rangle_x f_m,\quad (51)$$

where W_n is given by (13) with $\Phi = \Phi_n$. According to the results above, in the neighborhood of the equilibrium configuration of U_n the nonadiabatic terms on the right-hand side of (51) are of order κ^6 . This conclusion is at variance with the prediction of Landau and Lifshitz [9] that those terms should be of order κ^3 .

III. EXAMPLE

The best test of the general results and conclusions of the preceding section is their application to an exactly solvable problem exhibiting the main features of the more realistic model considered there. The simplest test example is

$$H = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2M} \frac{\partial^2}{\partial X^2} + \frac{x^2 + X^2}{2} + \beta x X,\quad (52)$$

where we identify the "electronic" operator

$$H_E = -\frac{1}{2} \frac{\partial^2}{\partial x^2} + \frac{x^2 + X^2}{2} + \beta x X,\quad (53)$$

and the "nuclear" kinetic-energy operator

$$T_N = -\frac{1}{2M} \frac{\partial^2}{\partial X^2}.\quad (54)$$

For simplicity we use units in which $\hbar = m = 1$ so that M stands for the ratio of the nuclear to the electronic mass and $\kappa = M^{-1/4} \ll 1$.

By means of a straightforward change of variables one transforms H into the sum of two uncoupled harmonic oscillators with unit mass and force constants given by

$$k_{\pm} = \frac{M + 1 \pm \sqrt{(M-1)^2 + 4M\beta^2}}{2M}.\quad (55)$$

The exact energy levels of the system are

$$E_{nv} = (n + \frac{1}{2})\sqrt{k_+} + (v + \frac{1}{2})\sqrt{k_-}, \quad n, v = 0, 1, \dots,\quad (56)$$

where n and v represent electronic and vibrational quantum numbers, respectively, because $k_+ \gg k_-$. The per-

turbation expansion of (56) produces only even powers of κ in agreement with the discussion in the preceding section,

$$E_{nv} = (n + \frac{1}{2}) \left[1 + \frac{\beta^2}{2} \kappa^4 - \frac{\beta^2(5\beta^2 - 4)}{8} \kappa^8 + \dots \right] + (v + \frac{1}{2}) \sqrt{1 - \beta^2} \left[\kappa^2 - \frac{\beta^2}{2} \kappa^6 + \dots \right]. \quad (57)$$

This series shows plainly that n and v play the role of the electronic and nuclear quantum numbers, respectively, because $E_{nv} - E_{nv'} = O(\kappa^2)$. The second term in the right-hand side of (57) vanishes when $\beta = \pm 1$ disclosing the fact that the potential energy function exhibits a saddle point for such values of the coupling constant (there are bound states only when $\beta^2 < 1$). The energies of this model have branch points of unit modulus on the complex M plane so that the perturbation series converges for all $\kappa < 1$.

In terms of the variable $s = x + \beta X$ the electronic operator

$$H_E = -\frac{1}{2} \frac{\partial^2}{\partial s^2} + \frac{s^2}{2} + \frac{1 - \beta^2}{2} X^2 \quad (58)$$

describes a harmonic oscillator with unit mass and force constant. Therefore, the electronic states $\Phi_n(x, X) = \Phi_n(s)$ are harmonic-oscillator eigenfunctions and all the electronic energies

$$U_n(X) = n + \frac{1}{2} + \frac{1 - \beta^2}{2} X^2 \quad (59)$$

have a minimum at the same nuclear configuration $X = 0$. According to (59) the nuclear states $g_v(X)$ are eigenfunctions of a harmonic oscillator with frequency $\sqrt{1 - \beta^2}$ and the Born-Oppenheimer energies are

$$\mathcal{E}_{nv} = (v + \frac{1}{2}) \sqrt{1 - \beta^2} \kappa^2 + n + \frac{1}{2}. \quad (60)$$

It follows from (57) and (60) that $E_{nv} - \mathcal{E}_{nv} = O(\kappa^4)$ in agreement with (19).

To calculate the correction of fourth order to the energy we take into account that $\partial \Phi / \partial X = \beta d \Phi / ds$ which enables us to write

$$W_n = \frac{\beta^2}{2M} \left\langle \frac{d\Phi_n}{ds} \left| \frac{d\Phi_n}{ds} \right\rangle_s = \frac{\beta^2}{2M} (n + \frac{1}{2}) = W_n^{(4)} \kappa^4. \quad (61)$$

The change of nuclear variable is $X = \kappa u$ and noticing that $s = x + \kappa \beta u$ we write

$$\frac{\partial \Phi_n(x, X)}{\partial \kappa} = \frac{\partial \Phi_n(s)}{\partial s} \beta u \quad (62)$$

and

$$\frac{\partial \Phi_n^{(1)}}{\partial u} = \beta \frac{\partial \Phi_n(x)}{\partial x} = \frac{\beta}{\sqrt{2}} (\sqrt{n} \Phi_{n-1} - \sqrt{n+1} \Phi_{n+1}), \quad (63)$$

which is necessary for the calculation of the perturbation correction of sixth order.

To construct the effective vibrational Hamiltonian we

need the nonadiabatic kinetic operator

$$\mathcal{T} = -\frac{\beta^2}{2} \frac{\partial^2}{\partial u^2}, \quad (64)$$

which follows from (63) and the corresponding expressions of the preceding section, the series expansion for the Born-Oppenheimer potential

$$U^{(2)} = \frac{1 - \beta^2}{2} u^2, \quad U^{(j)} = 0, \quad j > 2, \quad (65)$$

and the series expansion for the adiabatic potential

$$W^{(4)} = \frac{\beta^2}{2} (n + \frac{1}{2}), \quad W^{(j)} = 0, \quad j \neq 4. \quad (66)$$

The eigenvalues of the resulting operator

$$H_{\text{vib}} = -\frac{1}{2} (1 - \kappa^4 \beta^2) \frac{\partial^2}{\partial u^2} + \frac{1 - \beta^2}{2} u^2 + \frac{\kappa^2 \beta^2}{2} (n + \frac{1}{2}) \quad (67)$$

and

$$\begin{aligned} \varepsilon_{nv} &= \frac{\kappa^2 \beta^2}{2} (n + \frac{1}{2}) + (v + \frac{1}{2}) \sqrt{1 - \beta^2} \sqrt{1 - \kappa^4 \beta^2} \\ &= \frac{\kappa^2 \beta^2}{2} (n + \frac{1}{2}) + (v + \frac{1}{2}) \sqrt{1 - \beta^2} \left[1 - \frac{\kappa^4 \beta^2}{2} \right] + O(\kappa^8). \end{aligned} \quad (68)$$

The approximate energies $E_{nv}^{\text{app}} = (n + \frac{1}{2}) + \kappa^2 \varepsilon_{nv}$ agree with (57) up to $O(\kappa^6)$ thus confirming our general results.

The adiabatic energy E_{nv}^A is just the Born-Oppenheimer energy (60) plus the constant adiabatic term (61). One easily obtains $E_{nv} - E_{nv}^A = O(\kappa^6)$ in agreement with (20). Furthermore, this simple example also enables us to verify the inequalities discussed in the preceding section: $\mathcal{E}_{00} < E_{00} < E_{00}^A$.

IV. FURTHER COMMENTS AND CONCLUSIONS

We think that the perturbation method developed in Sec. II is more suitable than the original procedure of Born and Huang [5] for the systematic analysis of perturbation corrections of large order in κ . Our two main equations (9) and (14) greatly simplify the application of perturbation theory because they reflect beforehand the form of the results of Born and Huang [5]. Although entirely equivalent to its predecessor the present approach reveals in a simpler and clearer way the relative accuracy of the various approximations usually made. Notice, for example, that by just simple inspection of the main equations one derives the important results in Eqs. (19) and (20) or compare the present calculation of the energy correction of fourth order with the corresponding treatment by Born and Huang [5]. Furthermore, present derivation of the corrections of fifth and sixth order and of the effective Hamiltonian for the nuclear motion that takes into account adiabatic and nonadiabatic effects is straightforward.

Our treatment is more general than that followed by Patterson [1] which applies to one nuclear degree of free-

dom. We have extended to any number of nuclei the proof that the nonadiabatic effects of lowest order are negative and linear in the vibrational quantum number.

In the case of a system of finite size (take a molecule as a representative example) one applies the change of variables $X_i = X_{0i} + \kappa u_i$ only to the degrees of freedom that define an equilibrium nuclear configuration. If one singles out the corresponding coordinates then the application of perturbation theory is straightforward following the lines indicated above. To this end one simply substitutes $\partial/\partial u_i$ for $\partial/\partial X_i$ and $\kappa^4 M/(mM_i)$ for $1/M_i$ everywhere to rewrite the Hamiltonian operator in a form suitable for perturbation theory.

Some time ago Herman and Asgharian [10] derived an effective Hamiltonian for the vibration-rotational energies of diatomic molecules by means of standard Rayleigh-Schrödinger perturbation theory that takes into account both adiabatic and nonadiabatic effects of order m/M through functions of the internuclear distance. Later, Bunker and Moss [11] obtained essentially the same results by means of a more rigorous but at the same time more difficult approach based on a properly modified contact transformation. The expansion of those functions in Taylor series about the equilibrium configuration gives rise to κ -power series showing that the effective vibration-rotational Hamiltonian operator

obtained by both Herman and Asgharian [10] and Bunker and Moss [11] contains corrections of higher order. It is precisely the change of nuclear coordinates discussed above followed by the appropriate expansions about the equilibrium configuration that allows the systematic collection of all the terms that depend on the mass ratio as powers of the perturbation parameter κ . For example, the coefficient K that introduces nonadiabatic effects into the effective kinetic-energy operator for the present model with one nuclear degree of freedom is closely related to the first nonvanishing term of the expansion of either of the functions $g_2^2(R)$ [10] or $\beta(R)$ [11] about equilibrium.

In general the adiabatic approximation allows the separation of degrees of freedom associated to fast and slow motions and is not restricted to the case in which one clearly identifies heavy and light particles. For example, the present method may be useful to treat vibrational problems in which some of the frequencies differ markedly from the others.

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