A Non-Born–Oppenheimer Effective Hamiltonian for the Analysis of Vibrational–Rotational and Rotational Spectra of Diatomic Molecules

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A non-Born–Oppenheimer effective Hamiltonian for diatomic molecules with optimal fitting parameters, i.e., determinable clusters of expansion coefficients of Born–Oppenheimer corrections, has been derived. The effective Hamiltonian has formally the same form as Dunham's Hamiltonian, except for additional corrections for successive ξ'^i terms of a series expansion of the rotational parameter $B(\xi')$, extending the determinacy of the optimal parameters, $\Delta_B{}^{\mathrm{a,b}}$, $\Delta_\omega{}^{\mathrm{a,b}}$, $\Delta_{ai\mathrm{q}}{}^{\mathrm{a,b}}$, $r_{i\mathrm{q}}{}^{\mathrm{a,b}}$, in general for $i = 1, 2, 3, \ldots$, if spectra of isotopomers of atoms A and B are analyzed simultaneously. The effective Hamiltonian provides a clear-cut understanding of determinable correction parameters; e.g., in Dunham-type potential fits to spectral transitions for the single isotopomer optimal parameters $\delta r_{i\mathrm{q}}$ ($i = 1, 2, \ldots$) for corrections of series expansion terms of $B(\xi')$ should explicitly be included. The physical significance of the optimal parameters as well as of conventional molecular parameters, B_e, $-D_\mathrm{e}$, H_e, ω_e, and $-\alpha_\mathrm{e}$, etc., is described.

The vibrational–rotational and rotational spectra of a diatomic molecular species for several vibrational states and various isotopomers are analyzed simultaneously, taking adiabatic and nonadiabatic corrections of the Born–Oppenheimer approximation into account.[1–6] Analytic expressions of Dunham's Y_{ij} with Δ_B and Δ_ω formalism for the Born–Oppenheimer corrections[7–9] have revealed that clusters of expansion coefficients for $Q(\xi)$, $R(\xi)$, and $S(\xi)$, called optimal fitting parameters, are determinable by an analysis of spectral transitions. Thus, the correction functions $Q(\xi)$, $R(\xi)$, and $S(\xi)$ can be determined separately[9] if one accepts Herman and Ogilvie's method to evaluate $R(\xi)$.[10] This approach of the spectral analysis has been applied to LiH[9] and HCl.[11]

A prospective non-Born–Oppenheimer effective Hamiltonian expressed with optimal parameters has been described qualitatively in Ref. 9: optimal parameters $\delta\Delta_B$, $\delta\Delta_\omega$, and $\delta\Delta_{ai\mathrm{q}}$ ($i = 1, 2, \ldots$) are corrections for the type of δp_i in $p_i(1 + \delta p_i)$ in which p_i represents one of B_e, ω_e, or a_i ($i = 1, 2, \ldots$), respectively, and $\delta r_{i\mathrm{q}}$ ($i = 1, 2, \ldots$) are those of successive ξ^i ($i = 1, 2, \ldots$) terms of a series expansion of the rotational parameter $B(\xi)$.[9] The quantity δx_i denotes $(m_\mathrm{e}/M_\mathrm{a})x_i{}^\mathrm{a} + (m_\mathrm{e}/M_\mathrm{b})x_i{}^\mathrm{b}$.

It has been left to derive an exact expression of the effective Hamiltonian with the optimal parameters. An analytic approach is necessary to generate the exact form of the Hamiltonian expressed with a correct coordinate.

Non-Born–Oppenheimer Effective Hamiltonian

An appropriate original effective Hamiltonian[1–5] ignoring orders higher than $\mathrm{O}(m_\mathrm{e}/M_i)$ in the electronic state $^1\Sigma$ yields a Schrödinger equation in terms of the variable $\xi = (r - r_\mathrm{e})/r_\mathrm{e}$ as

$$\begin{aligned}&\Bigg[-\frac{h^2}{8\pi^2\mu r_\mathrm{e}{}^2}\frac{\mathrm{d}}{\mathrm{d}\xi}\{1 + (m_\mathrm{e}/M_\mathrm{a})Q_\mathrm{a}(\xi)\\ &\quad + (m_\mathrm{e}/M_\mathrm{b})Q_\mathrm{b}(\xi)\}\frac{\mathrm{d}}{\mathrm{d}\xi} + \frac{h^2}{8\pi^2\mu r_\mathrm{e}{}^2(1+\xi)^2}\\ &\quad \times \{1 + (m_\mathrm{e}/M_\mathrm{a})R_\mathrm{a}(\xi) + (m_\mathrm{e}/M_\mathrm{b})R_\mathrm{b}(\xi)\}J(J+1)\\ &\quad + V(\xi) + (m_\mathrm{e}/M_\mathrm{a})S_\mathrm{a}(\xi) + (m_\mathrm{e}/M_\mathrm{b})S_\mathrm{b}(\xi)\Bigg]\psi_{vJ}(\xi)\\ &\quad = E_{vJ}\psi_{vJ}(\xi), \qquad (1)\end{aligned}$$

in which μ is the reduced mass of a molecule and M_a, M_b, and m_e are masses of atoms A, B, and an electron, respectively. Mass-independent functions, e.g., after Watson,[2] $Q_\mathrm{a,b}(\xi)$, $R_\mathrm{a,b}(\xi)$, and $S_\mathrm{a,b}(\xi)$ are non-Born–Oppenheimer terms for nonadiabatic vibrational, nonadiabatic rotational, and adiabatic effects, respectively.

Similar to Dunham's potential function,[12] functions $Q_\mathrm{a,b}(\xi)$, $R_\mathrm{a,b}(\xi)$, and $S_\mathrm{a,b}(\xi)$ are expressed as series expansions of ξ after Fernandez and Ogilvie.[4] The expansion coefficients of the ξ^i terms of $Q_\mathrm{a,b}(\xi)$, $R_\mathrm{a,b}(\xi)$, and $S_\mathrm{a,b}(\xi)$ are $q_i{}^\mathrm{a,b}$, $r_i{}^\mathrm{a,b}$, and $s_i{}^\mathrm{a,b}$, respectively.[7,9] With the appropriate manipulation of a Sturm–Liouville type operator in Eq. 1 for the vibrational kinetic energy followed by the removal of the adiabatic correction terms linear in ξ, the Shrödinger equation (Eq. 1) can be expressed in wavenumber units as[7,9]

$$\begin{aligned}&\Bigg[-B_\mathrm{e}\{1 + \delta q_0 + (4B_\mathrm{e}/\omega_\mathrm{e}^2)\delta s_1{}'\}\frac{\mathrm{d}^2}{\mathrm{d}\eta^2}\\ &\quad + \frac{B_\mathrm{e}\{1 + \delta r_0 + (4B_\mathrm{e}/\omega_\mathrm{e}^2)\delta s_1{}'\}}{(1+\eta)^2}\left(1 + \sum_{i=1}\delta r_i{}'\eta^i\right)J(J+1)\\ &\quad + \frac{\omega_\mathrm{e}^2}{4B_\mathrm{e}}\left(1 - (2B_\mathrm{e}/\omega_\mathrm{e}^2)\{(2 + 3a_1)\delta s_1{}' - 2\delta s_2{}'\}\right)\\ &\quad \times \eta^2\left(1 + \sum_{i=1}k_i\eta^i\right)\Bigg]\psi_{vJ}(\eta) = F_{vJ}\psi_{vJ}(\eta), \qquad (2)\end{aligned}$$

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in which

$$\eta = \{1 + (2B_\mathrm{e}/\omega_\mathrm{e}^2)\delta s_1{}'\}\xi + (2B_\mathrm{e}/\omega_\mathrm{e}^2)\delta s_1{}', \tag{3}$$

$$\delta r_i{}' = (m_\mathrm{e}/M_\mathrm{a})(r_i^\mathrm{a} - q_i^\mathrm{a}) + (m_\mathrm{e}/M_\mathrm{b})(r_i^\mathrm{b} - q_i^\mathrm{b}), \tag{4}$$

$$\delta s_i{}' = (m_\mathrm{e}/M_\mathrm{a})(s_i^\mathrm{a} + q_i^\mathrm{a} F_{vJ}) + (m_\mathrm{e}/M_\mathrm{b})(s_i^\mathrm{b} + q_i^\mathrm{b} F_{vJ}), \tag{5}$$

$$\begin{aligned} k_1 = a_1 - \delta q_1 - (2B_\mathrm{e}/\omega_\mathrm{e}^2)\{(a_1 - 3a_1{}^2 + 4a_2)\delta s_1{}' \\ + 2a_1\delta s_2{}' - 2\delta s_3{}'\}, \end{aligned} \tag{6}$$

and

$$\begin{aligned} k_2 = a_2 - a_1\delta q_1 - \delta q_2 - (2B_\mathrm{e}/\omega_\mathrm{e}^2)\{(2a_2 - 3a_1a_2 \\ + 5a_3)\delta s_1{}' + 2a_2\delta s_2{}' - 2\delta s_4{}'\}, \quad \text{etc.} \end{aligned} \tag{7}$$

A Dunham like treatment of Eq. 2 or a perturbation method of Kilpatrick[13] provides, after a replacement of F_{vJ} in Eq. 5 with a known power series expansion in $(v + 1/2)$ and $J(J + 1)$, an eigen value,

$$F_{vJ} = \sum_{i,j} Y_{ij}^*(v + 1/2)^i[J(J + 1)]^j, \tag{8}$$

in which $Y_{ij}{}^*$ $(= Y_{ij}{}^{*(0)} + Y_{ij}{}^{*(2)} + \ldots)$[14] includes the Born–Oppenheimer corrections to Dunham's original notation Y_{ij}. The $Y_{ij}{}^{*(0)}$ coefficients that are expressed with optimal correction parameters, $\delta\Delta_B$, $\delta\Delta_\omega$, $\delta\Delta_{a1\mathrm{q}}$, $\delta\Delta_{a2\mathrm{q}}$, …, $\delta r_{1\mathrm{q}}$, $\delta r_{2\mathrm{q}}$, $\delta r_{3\mathrm{q}}$, …, are given in Eqs. 36–43 of Ref. 9. The optimal correction parameters are determinable clusters of expansion coefficients of $q_i{}^\mathrm{a,b}$, $r_i{}^\mathrm{a,b}$, and $s_i{}^\mathrm{a,b}$.

Reference 9 has shown that a Schrödinger equation with $\tilde{R}_\mathrm{a,b}(\xi)$ and $\tilde{S}_\mathrm{a,b}(\xi)$ introduced from Watson's $\tilde{R}_\mathrm{a,b}(r)$ and $\tilde{S}_\mathrm{a,b}(r)$, respectively, as

$$\begin{aligned} &\Bigg[-\frac{h^2}{8\pi^2\mu r_\mathrm{e}^2}\frac{\mathrm{d}^2}{\mathrm{d}\xi^2} + \frac{h^2}{8\pi^2\mu r_\mathrm{e}^2(1+\xi)^2} \\ &\quad \times \{1 + (m_\mathrm{e}/M_\mathrm{a})\tilde{R}_\mathrm{a}(\xi) + (m_\mathrm{e}/M_\mathrm{b})\tilde{R}_\mathrm{b}(\xi)\}J(J+1) \\ &\quad + V(\xi) + (m_\mathrm{e}/M_\mathrm{a})\tilde{S}_\mathrm{a}(\xi) + (m_\mathrm{e}/M_\mathrm{b})\tilde{S}_\mathrm{b}(\xi)\Bigg]\psi_{vJ}(\xi) \\ &\quad = E_{vJ}\psi_{vJ}(\xi), \end{aligned} \tag{9}$$

provides just the same $Y_{ij}{}^{*(0)}$ as given in Eqs. 36–43 of Ref. 9. Definitions of $\tilde{R}_\mathrm{a,b}(\xi)$ and $\tilde{S}_\mathrm{a,b}(\xi)$ have been given in Ref. 9.

Some details are added to the discussion in Ref. 9. Expressing B_e and ω_e in units of cm^{-1}, $\tilde{r}_i{}^\mathrm{a,b}$ and $\tilde{s}_i{}^\mathrm{a,b}$ are given as

$$\begin{aligned} &\{\tilde{r}_0{}^\mathrm{a,b}, \tilde{r}_1{}^\mathrm{a,b}, \tilde{r}_2{}^\mathrm{a,b}, \tilde{r}_3{}^\mathrm{a,b}\} \\ &\quad = \{r_0{}^\mathrm{a,b} - P^\mathrm{a,b}(\xi_0), r_1{}^\mathrm{a,b} + P^\mathrm{a,b}(\xi_0) - q_0{}^\mathrm{a,b}, \\ &r_2{}^\mathrm{a,b} - P^\mathrm{a,b}(\xi_0) + q_0{}^\mathrm{a,b} - q_1{}^\mathrm{a,b}/2, r_3{}^\mathrm{a,b} \\ &\qquad + P^\mathrm{a,b}(\xi_0) - q_0{}^\mathrm{a,b} + q_1{}^\mathrm{a,b}/2 - q_2{}^\mathrm{a,b}/3\} \end{aligned} \tag{10}$$

and

$$\begin{aligned} &\{\tilde{s}_0{}^\mathrm{a,b}, \tilde{s}_1{}^\mathrm{a,b}, \tilde{s}_2{}^\mathrm{a,b}, \tilde{s}_3{}^\mathrm{a,b}, \tilde{s}_4{}^\mathrm{a,b}\} \\ &\quad = \{s_0{}^\mathrm{a,b}, s_1{}^\mathrm{a,b} + (hc\omega_\mathrm{e}{}^2/4B_\mathrm{e})P^\mathrm{a,b}(\xi_0), \\ &s_2{}^\mathrm{a,b} + (hc\omega_\mathrm{e}{}^2/4B_\mathrm{e})(3a_1P^\mathrm{a,b}(\xi_0)/2 + q_0{}^\mathrm{a,b}), \\ &s_3{}^\mathrm{a,b} + (hc\omega_\mathrm{e}{}^2/2B_\mathrm{e})(a_2P^\mathrm{a,b}(\xi_0) + 3a_1q_0{}^\mathrm{a,b}/4 + q_1{}^\mathrm{a,b}/4), \\ &s_4{}^\mathrm{a,b} + (hc\omega_\mathrm{e}{}^2/2B_\mathrm{e})(5a_3P^\mathrm{a,b}(\xi_0)/4 \\ &\qquad + a_2q_0{}^\mathrm{a,b} + 3a_1q_1{}^\mathrm{a,b}/8 + q_2{}^\mathrm{a,b}/6)\}, \end{aligned} \tag{11}$$

respectively. The quantity $P^\mathrm{a,b}(\xi_0)$ is the definite integral of $Q_\mathrm{a,b}(\xi)$ from ξ_0 to 0. The lower limit of integration ξ_0 that corresponds to Watson's r_0 in Ref. 2 is, in exact, $\xi_0{}^\mathrm{a}$ and $\xi_0{}^\mathrm{b}$, but the difference does not formally affect the conclusions of the present paper. In Ref. 9, $P(\xi_0{}^\mathrm{a,b})$ is a typing error. All $P(\xi_0{}^\mathrm{a,b})$ that appear in Ref. 9 should read $P^\mathrm{a,b}(\xi_0)$.

Although the above Eqs. 1–11, except 8 and 9, have been given in Ref. 9, we reproduce them in this paper to facilitate reproducing the results of the present calculation to generate the non-Born–Oppenheimer effective Hamiltonian. Watson's Hamiltonian with $\tilde{R}_\mathrm{a,b}(r)$ and $\tilde{S}_\mathrm{a,b}(r)$ has been given with the coordinate r but we are expressing it as given in Eq. 9 with the coordinate ξ. In our treatment, it is essential to write the expressions with ξ, not with r.

Setting $P^\mathrm{a,b}(\xi_0)$ to $r_0{}^\mathrm{a,b}$, a replacement of

$$\begin{aligned} &\{\delta q_0, \delta q_1, \delta q_2, \delta r_0, \delta r_1, \delta r_2, \delta r_3, \delta s_1, \delta s_2, \delta s_3, \delta s_4\} \\ &\quad \to \{0, 0, 0, 0, \delta\tilde{r}_1, \delta\tilde{r}_2, \delta\tilde{r}_3, \delta\tilde{s}_1, \delta\tilde{s}_2, \delta\tilde{s}_3, \delta\tilde{s}_4\} \end{aligned} \tag{12}$$

applied to $Y_{ij}{}^{*(0)}$ of Eqs. 36–43 in Ref. 9 yields exactly the same expressions as $Y_{ij}{}^{*(0)}$. This proves that the Schödinger equation 9 is identical to Eq. 2, i.e., to Eq. 1. Since $Y_{ij}{}^{*(0)}$ is defined in units of cm^{-1}, units of s_i and $\tilde{s}_i$ in the replacement 12 are in cm^{-1} after dividing the Schrödinger equation by hc. Therefore, the factor $hc\omega_\mathrm{e}{}^2/B_\mathrm{e}$ in Eq. 11 should be changed to $\omega_\mathrm{e}{}^2/B_\mathrm{e}$ when the replacement 12 is applied.

The above discussion indicates that replacement 12 applied to Eq. 2 generates an effective Hamiltonian expressed with optimal parameters. The step to derive the effective Hamiltonian is a simple but important one. After some treatments of equations a non-Born–Oppenheimer effective Hamiltonian is obtained as

$$\begin{aligned} H = &-B_\mathrm{e}(1 + \delta\Delta_B)\frac{\mathrm{d}^2}{\mathrm{d}\xi'^2} \\ &+ \frac{B_\mathrm{e}(1 + \delta\Delta_B)}{(1 + \xi')^2}\left(1 + \sum_{i=1}\delta r_{i\mathrm{q}}\xi'^i\right)J(J + 1) \\ &+ \frac{[\omega_\mathrm{e}(1 + \delta\Delta_\omega)]^2}{4B_\mathrm{e}(1 + \delta\Delta_B)}\xi'^2\left(1 + \sum_{i=1}a_i(1 + \delta\Delta_{ai\mathrm{q}})\xi'^i\right), \end{aligned} \tag{13}$$

in which

$$\xi' = (1 + \delta\Delta_B/2)\xi + \delta\Delta_B/2. \tag{14}$$

Equation 13 has formally the same form as Dunham's Hamiltonian[12] except for corrections for successive ξ'^i terms of the series expansion of the rotational parameter $B(\xi')$. The eigenvalue of the Schrödinger equation given by Eq. 13 is exactly the same as that of Eq. 2, and is written as Eq. 8 in units of cm^{-1}, in which the modified Dunham coefficients $Y_{ij}{}^{*(0)}$ are given in Eqs. 36–43 of Ref. 9 for ij = 01, 02, 03, 04, 10, 11, 12, and 20.

It is important that the effective Hamiltonian 13 is analytically generated with the correct coordinate ξ'. Equation 13 can also be derived directly from Eq. 9, converting the variable ξ to ξ' defined in Eq. 14. This substantiates that we can express

Eq. 13 in general for $i = 1, 2, \ldots$. The Hamiltonian 13 indicates that the minimum of the effective potential function occurs at $(1 - \delta\Delta_B/2)r_e$, which is equal to the internuclear distance determined from $B_e(1 + \delta\Delta_B)$. The optimal parameters $\delta\Delta_B$, $\delta\Delta_\omega$, and $\delta\Delta_{aiq}$ $(i = 1, 2, \ldots)$ are corrections for the Born–Oppenheimer breakdown of the type of δp_i in $p_i(1 + \delta p_i)$ in which p_i represents one of B_e, ω_e, or a_i, respectively, and δr_{iq} $(i = 1, 2, \ldots)$ are corrections for successive ξ'^i $(i = 1, 2, \ldots)$ terms of the series expansion of the rotational parameter $B(\xi')$.

Since molecular parameters $B_e(1 + \delta\Delta_B)$, $\omega_e(1 + \delta\Delta_\omega)$, $a_i(1 + \delta\Delta_{aiq})$ $(i = 1, 2, \ldots)$, and δr_{iq} $(i = 1, 2, \ldots)$ in the Hamiltonian 13 can be determined for each isotopomer, the optimal parameters, $\Delta_B^{a,b}$, $\Delta_\omega^{a,b}$, $\Delta_{aiq}^{a,b}$, and ${r_{iq}}^{a,b}$, are determinable in general for $i = 1, 2, 3, \ldots$. In Ref. 9, the determinacy of the optimal parameters was shown for $\delta\Delta_B$, $\delta\Delta_\omega$, $\delta\Delta_{a1q}$, $\delta\Delta_{a2q}$, δr_{1q}, δr_{2q}, and δr_{3q}. For the spectral analysis of a potential fit for an isotopomer in 100% natural abundance, corrections for the breakdown of the Born–Oppenheimer approximation have not been taken into account so far. Molecular parameters in Eq. 13 are $B_e(1 + \delta\Delta_B)$, $\omega_e(1 + \delta\Delta_\omega)$, $a_i(1 + \delta\Delta_{aiq})$ $(i = 1, 2, \ldots)$, and δr_{iq} $(i = 1, 2, \ldots)$. Therefore, the correction parameters δr_{iq} $(i = 1, 2, \ldots)$ should be included in such a fit. The physical significance of conventional molecular parameters $\{B_e, -D_e, H_e, \omega_e, -\alpha_e\}$,[15] for example, is

$$\begin{aligned}
&\{B_e(1 + \delta\Delta_B), -[4(B_e(1 + \delta\Delta_B))^3 \\
&\quad /(\omega_e(1 + \delta\Delta_\omega))^2](1 - \delta r_{1q}), \\
&[16(B_e(1 + \delta\Delta_B))^5/(\omega_e(1 + \delta\Delta_\omega))^4][3 + a_1(1 + \delta\Delta_{a1q}) \\
&\quad - (5 + 3a_1(1 + \delta\Delta_{a1q})/2)\delta r_{1q} + \delta r_{2q}], \omega_e(1 + \delta\Delta_\omega), \\
&[(B_e(1 + \delta\Delta_B))^2/(\omega_e(1 + \delta\Delta_\omega))][6 + 6a_1(1 + \delta\Delta_{a1q}) \\
&\quad - (4 + 3a_1(1 + \delta\Delta_{a1q}))\delta r_{1q} + 2\delta r_{2q}]\}. \qquad (15)
\end{aligned}$$

It should be noted that terms of orders higher than $O(m_e/M_{a,b})$ are ignored throughout. Expressions 15 shows that for a single isotopic species, determined values for molecular parameters, B_e, ω_e, and a_i, are those for $B_e(1 + \delta\Delta_B)$, $\omega_e(1 + \delta\Delta_\omega)$, and $a_i(1 + \delta\Delta_{aiq})$, respectively. A quantity D_e, for example, signifies neither $4(B_e(1 + \delta\Delta_B))^3/(\omega_e(1 + \delta\Delta_\omega))^2$ nor $4{B_e}^3/{\omega_e}^2$ but $4[(B_e(1 + \delta\Delta_B))^3/(\omega_e(1 + \delta\Delta_\omega))^2](1 - \delta r_{1q})$ if the non-Born–Oppenheimer treatment is considered.

Since the number of components in a set of the expansion coefficients ${q_i}^{a,b}$, ${r_i}^{a,b}$, and ${s_i}^{a,b}$, is larger than that of ${Y_{ij}}^{*(0)}$ determinable experimentally, the choice of a set of determinable clusters of the expansion coefficients is not unique. However, because of the physical significance of the corrections written above, the set of optimal parameters, $\delta\Delta_B$, $\delta\Delta_\omega$, $\delta\Delta_{aiq}$ $(i = 1, 2, \ldots)$, and δr_{iq} $(i = 1, 2, \ldots)$, is the most natural choice of clusters.

Watson[16] proposed R and S choices in his effective Hamiltonian, making $\tilde{R}_{a,b}(r_e)$ and $\tilde{S}_{a,b}{}'(r_e)$ vanish, respectively, by use of lower limits of integration r_{0i}. We showed in Ref. 9 that $P^{a,b}(\xi_0)$, the definite integral of $Q_{a,b}(\xi)$ from ξ_0 to 0, vanishes from an analytic expression of the eigenvalue F_{vJ}. Therefore both choices generate exactly the same result of F_{vJ}, and do not affect the present expression of the effective Hamiltonian 13.

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