[物理化学標準]

以下の問（1）～（7）に答えよ.

分子の微小な構造変化に対する電子基底状態のエネルギー変化を Born-Oppenheimer (BO) 近似と摂動論を使って考える.

はじめに，分子変形に伴う電子ハミルトニアンの変化を考える．分子の構造を指定する基準座標の一つを q とする．q が平衡構造における値 $q = Q_0$ から微小変位 Q だけ変化した場合を考える．平衡構造に対する電子ハミルトニアンを $\mathrm{H}(Q_0)$ とする．構造変化後の電子ハミルトニアンは微小変位 Q に関する二次までの Taylor 展開から

$$\mathrm{H}(Q_0 + Q) = \mathrm{H}(Q_0) + \left.\frac{\partial \mathrm{H}(q)}{\partial q}\right|_0 Q + \frac{1}{2}\left.\frac{\partial^2 \mathrm{H}(q)}{\partial q^2}\right|_0 Q^2 \qquad ①$$

と書ける．ただし，微分の添え字 0 は微分を $q = Q_0$ において評価することを示す．平衡構造における BO 電子波動関数 $\{\Psi_i\}$，それらの固有値 $\{E_i\}$ $(i = 0, 1, 2, \cdots)$ は既知とする．但し，$E_0 < E_1 < E_2 \cdots$ とする.

次に，式①に摂動理論を適用する．式①の右辺第一項 $\mathrm{H}(Q_0)$ をゼロ次のハミルトニアンとし，第二，第三項を摂動項とみなす．構造変化後の電子基底状態の電子エネルギー $E_0(Q_0 + Q)$は Q の二次までを考慮すると

$$E_0(Q_0 + Q) = E_0 + Q\langle\Psi_0|\left.\frac{\partial \mathrm{H}(q)}{\partial q}\right|_0|\Psi_0\rangle + \frac{1}{2}Q^2\langle\Psi_0|\left.\frac{\partial^2 \mathrm{H}(q)}{\partial q^2}\right|_0|\Psi_0\rangle + Q^2\sum_{i(\neq 0)}\frac{\left|\langle\Psi_0|\left.\frac{\partial \mathrm{H}(q)}{\partial q}\right|_0|\Psi_i\rangle\right|^2}{E_0 - E_i} \qquad ②$$

と計算される．ここで，記号 $\langle\Psi_0|\cdots|\Psi_i\rangle$ は全電子座標 τ に関する積分を表す．すなわち，$\langle\Psi_0|\cdots|\Psi_i\rangle = \int \mathrm{d}\tau\ \Psi_0(\tau)\cdots\Psi_i(\tau)$である.

（1） BO 近似とは何かを説明せよ.

（2） 式②右辺第二項は 0 とおける．その理由を簡潔に記せ.

（3） 変位 Q に対する力の定数 k を式②から導け．ここで，力の定数 k は変位 Q に対する電子エネルギーの変化が $(1/2)kQ^2$ で表されように定義されている.

（4） 前問（3）の答えに基づき，分子が q 方向へ変形しやすくなるための必要条件を述べよ．

（5） 分子が q 方向へ Q だけ微小変形した後の基底状態の波動関数 $\widetilde{\Psi_0}(Q)$ は摂動論から，$\{\Psi_i\}$，$\{E_i\}$ $(i = 0, 1, 2, \cdots)$ を使って式③で与えられる．式③で表される $\widetilde{\Psi_0}(Q)$ の物理化学的な意味を簡潔に説明せよ．

$$\widetilde{\Psi_0}(Q) = \Psi_0(Q_0) + Q \sum_{i(\neq 0)} \frac{\langle \Psi_0 | \left.\frac{\partial \mathrm{H}(q)}{\partial q}\right|_0 | \Psi_i \rangle}{E_0 - E_i} \Psi_i(Q_0) \qquad ③$$

但し，$\widetilde{\Psi_0}(Q)$は規格化されていない．

（6） 式③の $\langle \Psi_0 | \left.\frac{\partial \mathrm{H}(q)}{\partial q}\right|_0 | \Psi_i \rangle$ が i に依らず 0 でない定数となる場合，$\widetilde{\Psi_0}(Q)$ の成分として最も振幅の大きな励起 BO 波動関数は何か．簡潔な理由とともに答えよ．

図１に示すように，第一励起状態の波動関数 Ψ_1 が基底状態の波動関数 Ψ_0 からの一電子励起で記述できる場合，式②あるいは式③で $\langle \Psi_0 | \left.\frac{\partial \mathrm{H}(q)}{\partial q}\right|_0 | \Psi_1 \rangle \neq 0$となるためには

$$\Gamma_{\varphi_\mathrm{b}} \times \Gamma_{\varphi_\mathrm{a}} \supset \Gamma_q \qquad ④$$

が必要である．ここで，Γ_X は物理量 X が従う既約表現を表す．

（7） 式④で表される条件を使って，折れ線形（C_{2v}構造）の H_2O 分子の O-H 結合の解離反応を解析する．基底状態に対する分子軌道と基準座標の性質を図２に示す．また，表１は点群 C_{2v} の指標表である．これらを参考にして，O-H 結合の解離反応に関与すると考えられる基準振動モードを推定せよ．また，その理由を簡潔に記せ．

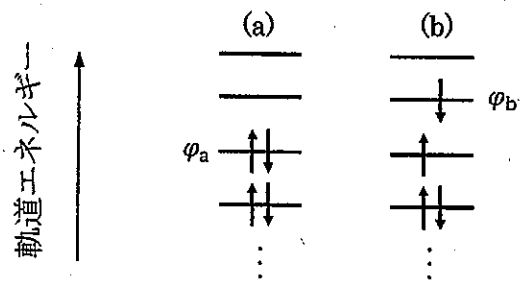

図１．基底状態の電子配置(a)と第一励起状態の電子配置(b)．第一励起状態が基底状態の最高被占軌道（φ_a）から最低空軌道（φ_b）への一電子励起で記述できることを示している．矢印はスピン状態の異なる電子を表す．

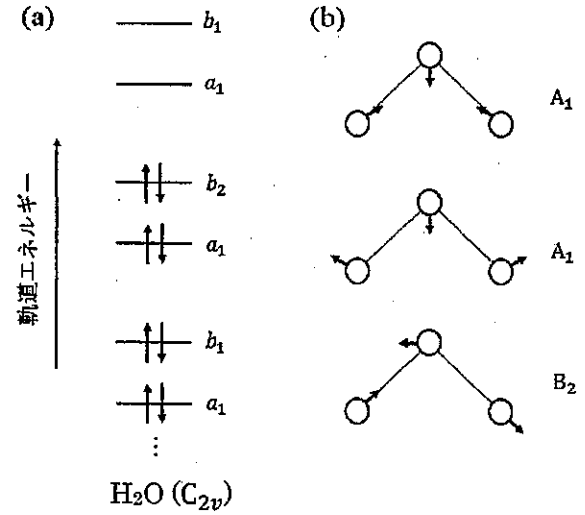

図２．折れ線形（C_{2v}構造）の H_2O 分子を考えた場合の (a) 最高被占軌道付近の軌道エネルギーとその対称性．矢印はスピン状態の異なる電子を表す．(b) 基準振動とその対称性．

表１．点群 C_{2v} の指標表

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h=4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	zx
B_2	1	−1	−1	1	y, R_z	yz

[Physical Chemistry: Standard]

Answer problems (1) through (7).

Consider a variation of the electronic ground-state energy of a molecule associated with a small structural change based on the Born-Oppenheimer (BO) approximation and the perturbation theory.

First, consider the variation of the electronic Hamiltonian associated with the structural change. Assume that a coordinate q is one of the normal coordinates that specifies the geometrical structure of a molecule. Consider the case where q changes by a small displacement Q from its equilibrium value $q = Q_0$. The electronic Hamiltonian of the molecule for the equilibrium structure is represented by $\mathrm{H}(Q_0)$. Within the second order Taylor expansion with respect to the small displacement Q, the electronic Hamiltonian after the structural change can be written as

$$\mathrm{H}(Q_0 + Q) = \mathrm{H}(Q_0) + \left.\frac{\partial \mathrm{H}(q)}{\partial q}\right|_0 Q + \frac{1}{2}\left.\frac{\partial^2 \mathrm{H}(q)}{\partial q^2}\right|_0 Q^2, \qquad ①$$

where the subscript 0 for the differentiation means that the derivative is evaluated at $q = Q_0$. The BO electronic wavefunctions associated with the equilibrium structure denoted by $\{\Psi_i\}$ and their eigenvalues denoted by $\{E_i\}$ $(i = 0, 1, 2, \cdots)$ are assumed to be known, where $E_0 < E_1 < E_2 < \cdots$.

Next, apply the perturbation theory to equation ①. Take the first term in the right-hand side of equation ①, $\mathrm{H}(Q_0)$, as the zeroth order Hamiltonian and the second and the third terms as perturbations. The ground-state electronic energy $E_0(Q_0 + Q)$ after the structural change is calculated within the second order of Q by

$$E_0(Q_0 + Q) = E_0 + Q\,\langle\Psi_0|\left.\frac{\partial \mathrm{H}(q)}{\partial q}\right|_0|\Psi_0\rangle + \frac{1}{2}Q^2\langle\Psi_0|\left.\frac{\partial^2 \mathrm{H}(q)}{\partial q^2}\right|_0|\Psi_0\rangle + Q^2\sum_{i(\neq 0)}\frac{\left|\langle\Psi_0|\left.\frac{\partial \mathrm{H}(q)}{\partial q}\right|_0|\Psi_i\rangle\right|^2}{E_0 - E_i}. \qquad ②$$

Here a notation $\langle\Psi_0|\cdots|\Psi_i\rangle$ is used to represent the integrations with respect to all the electron coordinates τ, i.e., $\langle\Psi_0|\cdots|\Psi_i\rangle = \int \mathrm{d}\tau\ \Psi_0(\tau)\cdots\Psi_i(\tau)$.

(1) Explain the meaning of the BO approximation.

(2) The second term on the right-hand side of equation ② can be set to be 0. Briefly explain the reason why it can be.

(3) Derive the force constant k for the displacement Q from equation ②. The force constant k is defined to represent the change of the electronic energy associated with the displacement Q by $(1/2)kQ^2$.

(4) Based on the answer to the problem (3), show the necessary condition that allows the molecular deformation along the q direction to become easier.

(5) According to the perturbation theory, the ground-state wavefunction, $\widetilde{\Psi_0}(Q)$, after the molecular deformation by the small displacement of Q, is represented as equation ③ in terms of $\{\Psi_i\}$ and $\{E_i\}$ $(i = 0, 1, 2, \cdots)$. Briefly explain the physicochemical meaning of the wavefunction represented by $\widetilde{\Psi_0}(Q)$.

$$\widetilde{\Psi_0}(Q) = \Psi_0(Q_0) + Q \sum_{i(\neq 0)} \frac{\langle \Psi_0 | \left.\frac{\partial \mathrm{H}(q)}{\partial q}\right|_0 | \Psi_i \rangle}{E_0 - E_i} \Psi_i(Q_0), \qquad ③$$

where $\widetilde{\Psi_0}(Q)$ is not normalized.

(6) If the terms $\langle \Psi_0 | \left.\frac{\partial \mathrm{H}(q)}{\partial q}\right|_0 | \Psi_i \rangle$ appearing in equation ③ are assumed to be a non-zero constant independent of i, which excited BO wavefunction will have the largest amplitude as a component of $\widetilde{\Psi_0}(Q)$? Answer with a brief explanation.

As is shown in Figure 1, if the first-excited-state wavefunction Ψ_1 is described by a single electron excitation from the ground-state wavefunction Ψ_0, equation ④ should hold to obtain $\langle \Psi_0 | \left.\frac{\partial \mathrm{H}(q)}{\partial q}\right|_0 | \Psi_1 \rangle \neq 0$ in equation ② or ③;

$$\Gamma_{\varphi_b} \times \Gamma_{\varphi_a} \supset \Gamma_{q}, \qquad ④$$

where Γ_X represents the irreducible representation of the physical quantity X.

(7) Using the above condition represented by equation ④, analyze the dissociation reaction of O-H bond of a H_2O molecule having the bent (C_{2v}) structure. The properties of the molecular orbitals in the ground state and the normal coordinates are shown in Figure 2. Table 1 shows the character table for the C_{2v} point group. Referring to these pieces of information, find a vibrational normal mode which can contribute to the dissociation reaction of O-H bond. Also, briefly explain the reason for that answer.

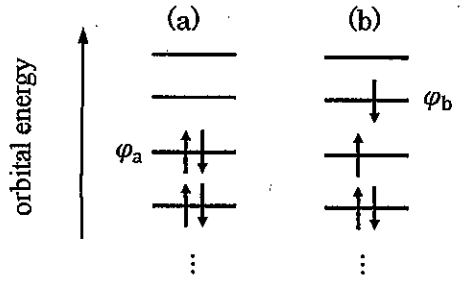

Figure 1. The configurations of the ground state (a) and the first excited state (b), respectively, showing that the first excited state is represented by the single electron excitation from the highest occupied molecular orbital (φ_a) to the lowest unoccupied molecular orbital (φ_b) of the ground state. The arrow indicates an electron with different spin states.

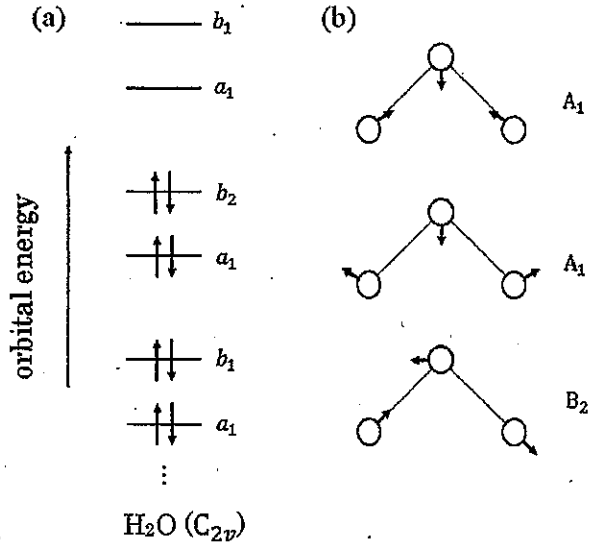

Figure 2. (a) The orbital energies and their symmetry near the highest occupied molecular orbital for a H_2O molecule in a bent (C_{2v}) structure. The arrow indicates an electron with different spin states. (b) The normal modes and their symmetry.

Table 1. Character table for the point group C_{2v}.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h=4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	zx
B_2	1	−1	−1	1	y, R_z	yz

問題訂正

科目名：物理化学標準
Subject: Physical Chemistry Standard

表1最下段　表記訂正
誤）*y,Rz*
正）*y,Rx*

Table 1 bottom, correction
Incorrect) *y,Rz*
Correct) *y,Rx*