

The dynamical Stark effect in diatomic molecules

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The effect of a variable electric field on the rotational and vibrational-rotational states of diatomic molecules is investigated under the assumption that the frequency of the field greatly exceeds the frequency of molecular rotation. In this case the variable potential can be approximately replaced by a constant effective potential, which is the analog of the Kapitza potential in the classical mechanics. The quasienergy spectrum of the molecule is calculated and the possibility of its experimental determination is discussed.

The static Stark effect in molecules has been well investigated for both weak^[1,2] and strong^[3-5] electric fields. The dynamical Stark effect in molecules was investigated by Autler and Townes^[6] for fields whose frequencies were substantially smaller than the rotational frequency of the molecule. Examination of the dynamical Stark effect in the infrared region is of interest in connection with the numerous investigations in recent years which have been devoted to the effects of laser radiation on molecules. The effect of a variable electric field on the rotational and vibrational states of a diatomic molecule is investigated in the present article under the assumption that the frequency of the field is of the same order as the molecule's vibrational frequency and considerably exceeds the rotational frequency of the molecule. This assumption is well satisfied, for example, in the case of diatomic molecules which are exposed to the radiation from a CO₂ laser.

The large difference between the frequency of the field and the rotational frequency of the molecule allows us to use the basic idea of Kapitza's method,^[7-9] namely, to replace the variable external field by a certain effective potential. The energy levels, which are obtained upon solving the Schrödinger equation with such an effective potential, undergo an additional "vibrating" motion, i.e., they undergo small-amplitude, high-frequency (the frequency of the field) displacements about some average position.

The behavior of a rigid rotator in an alternating electric field is investigated in the first part of the article; in the second part the treatment also takes vibrations into account under the assumption that the frequency of the external field is not in resonance with the vibrational frequency of the molecule. The concept of quasienergy, which was first introduced in the articles by Zel'dovich^[10] and Ritus^[11] and which is discussed in detail in the review article by Zel'dovich,^[12] turns out to be extremely useful for investigation of the vibrating rotator.

1. THE RIGID ROTATOR

The equation describing the rotation of a diatomic molecule with dipole moment μ_0 in the presence of a variable electric field $E \cos \omega t$ has the form

$$(H_r - U_0 \cos \omega t \cos \theta) \Psi = i\hbar \frac{\partial \Psi}{\partial t}, \quad (1)$$

$$H_r = -hcB_e \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right), \quad (2)$$

where H_r is the operator describing the free rotation of a rigid rotator with rotational constant B_e , $U_0 = \mu_0 E$,

and θ is the angle between the direction of the field and the axis of the molecule. If the frequency of the external field is appreciably greater than the characteristic rotational frequencies of the molecule, then in the Hamiltonian of Eq. (1) the terms naturally divide into "fast" and "slow" parts ($U_0 \cos \omega t \cos \theta$ and H_r).

From physical considerations (and in analogy with the adiabatic approximation) one can anticipate that the wave function will have the form of the product of a rapidly oscillating function times a function slowly varying in time. One can determine the rapidly oscillating part by considering Eq. (1) without the slowly varying terms, i.e., without the rotational Hamiltonian H_r . We shall seek then the wave function in the following form:

$$\Psi(\theta, \varphi, t) = \exp\left(-i \frac{U_0}{\hbar \omega} \sin \omega t \cos \theta\right) \Psi_r(\theta, \varphi, t), \quad (3)$$

where, by assumption, $\Psi_r(\theta, \varphi, t)$ is a function slowly varying in time. Substituting (3) into Eq. (1), we obtain

$$H_r \Psi_r = i\hbar \frac{\partial \Psi_r}{\partial t},$$

$$\begin{aligned} H_r &= \exp\left(i \frac{U_0}{\hbar \omega} \sin \omega t \cos \theta\right) H_r \exp\left(-i \frac{U_0}{\hbar \omega} \sin \omega t \cos \theta\right) \\ &= H_r - 2i\hbar c \frac{B_e U_0}{\hbar \omega} \sin \omega t \left(\cos \theta + \sin \theta \frac{\partial}{\partial \theta}\right) + \hbar c \frac{B_e U_0^2}{\hbar^2 \omega^2} \sin^2 \omega t \sin^2 \theta. \end{aligned}$$

Averaging over a small time interval (of the order of $2\pi/\omega$) and assuming that Ψ_r and $\partial \Psi_r / \partial t$ essentially do not change during this time interval, we obtain

$$(H_r + V_{\text{eff}}) \Psi_r = i\hbar \frac{\partial \Psi_r}{\partial t}, \quad (4)$$

where

$$V_{\text{eff}} = \hbar c B_e U_0^2 \sin^2 \theta / 2\hbar^2 \omega^2. \quad (5)$$

As is well known, if the potential is a periodic function of the time, the exact solution of the differential equation (1) can be written in the form (see^[13])

$$\Psi(t) = \hat{A}(t) \exp(-iH_{\text{eff}}t/\hbar) \Psi(0),$$

where the operator $\hat{A}(t)$ is periodic:

$$\hat{A}(t+2\pi/\omega) = \hat{A}(t),$$

and H_{eff} is a time-independent operator. In the approximation we are using, these operators are given by

$$\hat{A}(t) = \exp\left(-i \frac{U_0}{\hbar \omega} \sin \omega t \cos \theta\right), \quad H_{\text{eff}} = H_r + V_{\text{eff}}. \quad (6)$$

The more rigorous derivation, which is given in the Appendix, shows that expression (6) for the operator $\hat{A}(t)$ characterizing the fast periodic oscillations is correct to terms of order $U_0/\hbar\omega$, but the expression for

H_{eff} is correct up to and including terms of order $(U_0/\hbar\omega)^2$. Thus, it makes sense to only consider the effective potential H_{eff} in first-order perturbation theory. It is easy to see that the effective potential (5) agrees with the potential obtained from Kapitza's method.^{[7-9]1)} The derivation of Eq. (4) given above and the derivation given in the Appendix justify the use of this method in quantum mechanics and indicate the limits of its validity.

Equation (4) has stationary solutions of the form $\Psi_{\mathbf{r}} = \exp(-i\epsilon_{\mathbf{r}}t/\hbar) \times \chi_{\mathbf{r}}(\theta, \varphi)$, where $\epsilon_{\mathbf{r}}$ and $\chi_{\mathbf{r}}(\theta, \varphi)$ are the eigenvalues and eigenfunctions of the operator H_{eff} . Finally we obtain the result that the solution of Eq. (1) has the form

$$\Psi(\theta, \varphi, t) = \exp(-i\epsilon_{\mathbf{r}}t/\hbar) u(\theta, \varphi, t), \quad (7)$$

where $u(\theta, \varphi, t)$ is a periodic function of the time:

$$u(\theta, \varphi, t) = \exp\left(-i \frac{U_0}{\hbar\omega} \sin \omega t \cos \theta\right) \chi_{\mathbf{r}}(\theta, \varphi).$$

The function (7) describes the state with quasi-energy $\epsilon_{\mathbf{r}}$ and Bloch amplitude u . With the aid of perturbation theory we obtain the following expression for $\epsilon_{\mathbf{r}}$, which is correct up to and including terms of order $B_e U_0^2/\hbar^2 \omega^2$:

$$\frac{\epsilon_{\mathbf{r}}}{\hbar c} = B_e J(J+1) + \frac{B_e U_0^2}{2 \hbar^2 \omega^2} \frac{2J^2 + 2J - 2 + 2M^2}{(2J+3)(2J-1)}. \quad (8)$$

Thus, under the influence of the effective potential there is a splitting of the rotational levels with respect to the magnetic quantum number M , but the magnitudes of these splittings are described by a formula which is not the same as the formula for the static Stark effect. It should, however, be understood that the resulting levels are not stationary levels, but correspond to quasi-energy levels.

2. THE VIBRATING ROTATORS

The Schrödinger equation for a diatomic molecule in the presence of an electric field $E \cos \omega t$ has the following form (we neglect the vibrational-rotational interaction and the anharmonicity of the vibrations):

$$[H_v + H_r - \mu(x) E \cos \omega t \cos \theta] \Psi = i\hbar \frac{\partial \Psi}{\partial t}; \quad (9)$$

$$H_v = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2,$$

where H_r is determined by formula (2), $\mu(x)$ is the dipole moment of the molecule, m is the reduced mass of the diatomic molecule, k is the force constant, and x denotes the displacement of the nuclei from their equilibrium positions. We expand $\mu(x)$ in a series in powers of x and confine our attention to the first two terms:

$$\mu(x) = \mu_0 + \mu_0' x.$$

In analogy with the case of the rigid rotator, let us first attempt to extract the rapidly oscillating part of the wave function. Therefore, we first consider the Schrödinger equation without the rotational terms:

$$[H_v - \mu(x) E \cos \omega t \cos \theta] \Psi = i\hbar \frac{\partial \Psi}{\partial t}. \quad (10)$$

Let us introduce the variable

$$y = xm^{1/2}/\hbar$$

and we also introduce the following notation:

$$\omega_0^2 = k/m, \quad U = U_0 \cos \theta = \mu_0 E \cos \theta, \quad f = f_0 \cos \theta = \mu_0' E \hbar \cos \theta / m^{1/2}.$$

Then Eq. (10) takes the form

$$\left[-\frac{1}{2} \frac{d^2}{dy^2} + \frac{1}{2} \hbar^2 \omega_0^2 y^2 - U_0 \cos \omega t - f y \cos \omega t \right] \Psi = i\hbar \frac{\partial \Psi}{\partial t}. \quad (11)$$

Let us make the following substitution:

$$\Psi(y, t) = \exp(-iU_0 \sin \omega t / \hbar \omega) \tilde{\Psi}(y, t).$$

We then obtain the following equation for the function $\tilde{\Psi}$:

$$\left[-\frac{1}{2} \frac{d^2}{dy^2} + \frac{1}{2} \hbar^2 \omega_0^2 y^2 - f y \cos \omega t \right] \tilde{\Psi} = i\hbar \frac{\partial \tilde{\Psi}}{\partial t}. \quad (12)$$

This equation admits an exact solution which can be represented in the following form:^[15,16]

$$\tilde{\Psi}_n(y, t) = \exp(-i\epsilon_n t / \hbar) \varphi_n(y, t),$$

where ϵ_n is the quasienergy,

$$\begin{aligned} \epsilon_n &= \epsilon_n^{(0)} + \Delta\epsilon = \hbar\omega_0(n+1/2) + f^2/4\hbar^2(\omega^2 - \omega_0^2), \\ \varphi_n(y, t) &= \Phi_n(y - a \cos \theta) \exp(-ib \cos^2 \theta), \end{aligned}$$

Φ_n is the n -th Hermite polynomial,

$$a = \frac{f_0 \cos \omega t}{\hbar^2(\omega_0^2 - \omega^2)}, \quad b = \frac{f_0^2 \sin^2 2\omega t}{\hbar^3 \omega (\omega^2 - \omega_0^2)}.$$

Let us represent the solution of Eq. (11) in the following form:

$$\Psi(y, t) = \Psi_{hf} \exp(-i\Delta\epsilon t / \hbar),$$

$$\Psi_{hf}(y, t) = \exp\left(-i \frac{U_0}{\hbar\omega} \sin \omega t \cos \theta\right) \exp\left(-\frac{i\epsilon_n^{(0)} t}{\hbar}\right) \varphi_n(y, t).$$

We assume that the inequality

$$\Delta\epsilon / \hbar\omega \ll 1.$$

is satisfied. Then the quantity $\exp(-i\Delta\epsilon t / \hbar)$ is a slowly varying function of the time in comparison with Ψ_{hf} . It is obvious that the function Ψ_{hf} satisfies the equation

$$(H_v - U \cos \omega t - \Delta\epsilon) \Psi_{hf} = i\hbar \frac{\partial \Psi_{hf}}{\partial t}.$$

We seek the solution of Eq. (9) in the following "adiabatic" form:

$$\Psi = \Psi_{hf} \Psi_r(\theta, \varphi, t), \quad (13)$$

where Ψ_r is the rotational function, which varies slowly with the time. Substituting (13) into (9), multiplying by Ψ_{hf}^* from the left, and integrating over y , we obtain the equation

$$[\langle H_r \rangle + \Delta\epsilon(\theta)] \Psi_r(\theta, \varphi, t) = i\hbar \frac{\partial \Psi_r}{\partial t},$$

$$\langle H_r \rangle = \int \Psi_{hf}^* H_r \Psi_{hf} dy.$$

Taking the explicit dependence of Ψ_{hf} on θ into account and averaging over a small time interval, just as was done in the case of the rigid rotator, we obtain

$$[H_r + V_{\text{eff}} + \epsilon(\theta)] \Psi_r = i\hbar \frac{\partial \Psi_r}{\partial t},$$

where

$$\begin{aligned} V_{\text{eff}} &= \hbar c B_e (A_n \sin^2 \theta + B \sin^2 2\theta), \\ A_n &= \frac{1}{2} \frac{U_0^2}{\hbar^2 \omega^2} + \frac{\omega_0 f^2}{\hbar^2 (\omega^2 - \omega_0^2)^2} \left[\frac{1}{16} \left(n + \frac{1}{2} \right) - \frac{1}{2} - \frac{n^{3/2}}{2^{1/2}} \right], \\ B &= \frac{1}{16} \frac{f^4}{\hbar^4 \omega^2 (\omega^2 - \omega_0^2)^2}. \end{aligned}$$

Because of the assumption made above concerning the smallness of $f^2/\hbar^2(\omega^2 - \omega_0^2)$, we shall neglect the quantity B in what follows. Then, representing $\Delta\epsilon(\theta)$ in the form

$$\Delta\epsilon(\theta) = \frac{f_0^2}{4\hbar^2(\omega^2 - \omega_0^2)} (1 - \sin^2 \theta),$$

we obtain

$$(H_r + U_{\text{eff}} + \Delta \epsilon_0) \Psi_r = i\hbar \frac{\partial \Psi_r}{\partial t};$$

$$U_{\text{eff}} = \left(hc B_e A_n - \frac{f_0^2}{4\hbar^2 (\omega^2 - \omega_0^2)} \right) \sin^2 \theta, \quad (14)$$

$$\Delta \epsilon_0 = \frac{f_0^2}{4\hbar^2 (\omega^2 - \omega_0^2)}.$$

Except for the constant $\Delta \epsilon_0$, Eq. (14) has the same form as the rotation equation (4) for the rigid rotator. Therefore

$$\Psi_r = \exp(-i\epsilon_r t/\hbar) \chi_r(\theta, \varphi), \quad (15)$$

$$\frac{\epsilon_r}{\hbar c} = B_e J(J+1) + \left[B_e A_n - \frac{f_0^2}{4\hbar^2 hc (\omega^2 - \omega_0^2)} \right] \frac{2J^2 + 2J - 2 + 2M^2}{(2J+3)(2J-1)} + \frac{\Delta \epsilon_0}{\hbar c}$$

Finally we obtain the result that the solution of Eq. (11) has the form

$$\Psi = \exp[-i(\epsilon_n^{(0)} + \epsilon_r)t/\hbar] u(y, \theta, \varphi, t),$$

where

$$u = \exp(-i\Delta \epsilon(\theta)t/\hbar) \Psi_{nr}(y, \theta, t) \chi_r(\theta, \varphi),$$

and $\epsilon_n^{(0)} + \epsilon_r$ is the quasienergy of the system under consideration.

3. ESTIMATES

In all of the estimates cited below we shall assume that the molecule is interacting with the radiation from a CO₂ laser, having a frequency $\omega \approx 19 \times 10^{13}$ Hz and creating an electric field intensity of 10^6 V/cm.

First let us consider a rigid rotator in the field produced by such a laser. In this connection the splitting of the rotational quasienergy levels is determined by the constant $B_e U_0^2 / 2\hbar^2 \omega^2$. For the HCl molecule we obtain ($\mu_0 = 1.09$ D, $B_e = 10.6$ cm⁻¹)

$$B_e U_0^2 / 2\hbar^2 \omega^2 \sim 0.3 \text{ cm}^{-1},$$

and for the CO molecule we obtain ($\mu_0 = 0.12$ D, $B_e = 1.93$ cm⁻¹)

$$B_e U_0^2 / 2\hbar^2 \omega^2 \sim 0.0001 \text{ cm}^{-1}.$$

With the vibrations taken into account, we obtain the following result for the HCl molecule ($\nu_0 = \omega_0 / 2\pi c = 2988$ cm⁻¹, $\mu' = 0.949$ D/Å):

$$A_n = 0.01 + 0.06 \left[\frac{1}{16} \left(n + \frac{1}{2} \right) - \frac{1}{2} - \frac{n^{3/2}}{2^{3/2}} \right],$$

$$\frac{f_0^2}{4\hbar^2 (\omega^2 - \omega_0^2) hc} = 0.02 \text{ cm}^{-1}.$$

Therefore, the magnitude of the splitting for the lowest vibrational levels is of the order of 0.1 cm⁻¹. For the CO molecule ($\nu_0 = 2168$ cm⁻¹, $\mu' = -3.07$ D/Å) we find

$$A_n = 0.00006 + 0.1 \left[\frac{1}{16} \left(n + \frac{1}{2} \right) - \frac{1}{2} - \frac{n^{3/2}}{2^{3/2}} \right],$$

$$\frac{f_0^2}{4\hbar^2 (\omega^2 - \omega_0^2) hc} = 10^{-4} \text{ cm}^{-1}$$

and the splitting of the rotational levels is on the order of 0.2 cm⁻¹.

4. CONCLUSION

The splitting of the rotational levels of the quasienergy, which has been considered in the present article, can be observed, for example, by investigating the absorption or emission spectra of a diatomic molecule in the presence of a laser field. The question of the emission and absorption by the quasienergy states in the

presence of a weak electromagnetic field is discussed in detail in the review article by Zel'dovich.^[12] One can briefly state the basic results in the following way. Light of frequency $\nu = (\epsilon_1 - \epsilon_2)\hbar + \hbar\omega p$, where p is an integer, is absorbed or emitted during the transition between the two quasienergy states ϵ_1 and ϵ_2 . The intensity of the individual components is determined by the coefficients in the expansion of the wave function for the quasienergy state in a Fourier series. Hence, it follows in particular that splitting of the usual vibrational-rotational bands will be observed in the absorption or emission spectra for a diatomic molecule in a variable electric field. The splitting is determined by formulas (8) and (15) and can be observed by the methods of microwave or infrared spectroscopy. The magnitude of this splitting can be used, for example, to accurately determine the field intensity in the laser beam.

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APPENDIX

In Kapitza's articles it was established that the effect of a rapidly varying force field on a classical particle can be approximately reduced to a certain time-independent pseudopotential (see^[7-9]). Let us indicate how the introduction of the Kapitza pseudopotential into quantum-mechanical problems can be justified.

We consider the Schrödinger equation for a system in a field which harmonically depends on the time:

$$[H_0(r) + \lambda V(r) \cos \omega t] \Psi = i\hbar \frac{\partial \Psi}{\partial t}. \quad (\text{A.1})$$

We shall be interested in the particular solution of this equation which arises from the eigenfunction $\Psi_n^{(0)}$ for the n -th level of the operator H_0 upon adiabatically switching on the external field. We shall assume that either the initial energy level $E_n^{(0)}$ of the operator H_0 is nondegenerate or else the unperturbed eigenfunctions $\Psi_n^{(0)}$ of the degenerate level are not mixed by the perturbation:

$$\langle \Psi_{n\alpha}^{(0)} | V | \Psi_{n\beta}^{(0)} \rangle = 0 \text{ if } \alpha \neq \beta.$$

As is well known, the following expression is obtained for the wave function in first order perturbation theory:^[17]

$$\Psi(r, t) = \Psi_n^{(0)} \exp(-iE_n^{(0)} t/\hbar) + \frac{\lambda}{2} \exp\left(-\frac{iE_n^{(0)} t}{\hbar}\right) \left\{ \sum_k \Psi_k^{(0)} \left[\frac{\langle \Psi_k^{(0)} | V | \Psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)} - \hbar\omega} e^{i\omega t} + \frac{\langle \Psi_k^{(0)} | V | \Psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)} + \hbar\omega} e^{-i\omega t} \right] \right\} + O(\lambda^2).$$

Now let us assume that for all levels for which the matrix element of the perturbation operator $V_{kn} \equiv \langle \Psi_k^{(0)} | V | \Psi_n^{(0)} \rangle$ is noticeably different from zero, the frequency of the external field is very much greater than the transition frequency $\omega_{kn} = |E_k^{(0)} - E_n^{(0)}|/\hbar$: $\omega \gg \omega_{kn}$ if $V_{kn} \neq 0$. Then, in the denominators appearing in formula (A.2) one can neglect the quantities $E_n^{(0)} - E_k^{(0)}$ in comparison with $\hbar\omega$, and the effective parameter characterizing the smallness of the perturbation theory will be the ratio λ/ω .

Now let us demonstrate that, under the assumption which has been made concerning the frequency of the external field, its influence can be calculated to within terms of order λ^2/ω^2 inclusively by introducing the static pseudopotential. In order to prove this, we make the following substitution in Eq. (A.1):

$$\Psi = \exp\left(-i \frac{\lambda V}{\hbar \omega} \sin \omega t\right) f(\mathbf{r}, t).$$

The function $f(\mathbf{r}, t)$ is the solution of the equation

$$\hat{H}f = i\hbar \frac{\partial f}{\partial t},$$

where

$$\hat{H} = \exp\left(i \frac{\lambda V}{\hbar \omega} \sin \omega t\right) H_0 \exp\left(-i \frac{\lambda V}{\hbar \omega} \sin \omega t\right) = H_0 + i \frac{\lambda}{\hbar \omega} [V, H_0] \sin \omega t - \frac{1}{2} \frac{\lambda^2}{(\hbar \omega)^2} [V, [V, H_0]] \sin^2 \omega t + O\left(\frac{\lambda^3}{\omega^3}\right).$$

To eliminate the term of order λ/ω in the Hamiltonian \hat{H} , we make an additional substitution:

$$f = \exp\left\{i \frac{\lambda^2 \cos \omega t}{\hbar^2 \omega^2} (i[V, H_0])\right\} g(\mathbf{r}, t).$$

Correct to terms of order λ^2/ω^2 inclusively, the equation for the function g takes the form

$$\begin{aligned} i\hbar \frac{\partial g}{\partial t} &= \left\{ H_0 - \frac{1}{2} \frac{\lambda^2}{(\hbar \omega)^2} [V, [V, H_0]] \sin^2 \omega t \right. & (A.3) \\ &- \left. \frac{\lambda^2}{(\hbar \omega)^2} [H_0, [V, H_0]] \cos \omega t + O\left(\frac{\lambda^3}{\omega^3}\right) \right\} g(\mathbf{r}, t) \\ &= \left\{ H_0 - \frac{1}{4} \frac{\lambda^2}{(\hbar \omega)^2} [V, [V, H_0]] + \frac{\lambda^2}{(\hbar \omega)^2} [V, (V, H_0)] \frac{1}{4} \cos 2\omega t \right. \\ &- \left. \frac{\lambda}{(\hbar \omega)^2} [H_0, [V, H_0]] \cos \omega t + O\left(\frac{\lambda^3}{\omega^3}\right) \right\} g(\mathbf{r}, t). \end{aligned}$$

Considering the variable terms in the last part of Eq. (A.3) as a perturbation, in accordance with Eq. (A.2) we find that the corrections to the function $g(\mathbf{r}, t)$ induced by them will be of order λ^3/ω^3 and, therefore, they do not need to be considered in the assumed approximation.

Let us state the final result: The wave function of the system is given by

$$\Psi = \exp\left(i \frac{\lambda V}{\hbar \omega} \sin \omega t\right) \exp\left\{i \frac{\lambda^2 \cos \omega t}{\hbar^2 \omega^2} (i[V, H_0])\right\} g(\mathbf{r}, t) + O\left(\frac{\lambda^3}{\omega^3}\right), \quad (A.4)$$

where g is the solution of the Schrödinger equation with the time-independent Hamiltonian

$$H_{\text{eff}} = H_0 - \frac{1}{4} \frac{\lambda^2}{(\hbar \omega)^2} [V, [V, H_0]]. \quad (A.5)$$

This, the evolution of the system in a rapidly varying field consists of a slow motion (related to the variation of the function $g(\mathbf{r}, t)$), on which is imposed a rapid "vibration," described by the exponential factors in Eq. (A.4). This is completely analogous to the corresponding classical result. In the one-dimensional case, when

$$H_0 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x),$$

we obtain the well known expression for the Kapitza pseudopotential:

$$V_{\text{eff}} = \frac{1}{4m\omega^2} \left(\lambda \frac{dU}{dx} \right)^2.$$

For the rigid rotator we obtain an expression which corresponds to the effective potential cited in the main text of this article (see formula (4):

$$V_{\text{eff}} = \frac{\hbar c B_0 U_0^2 \lambda^2}{2\hbar^2 \omega^2} \sin^2 \theta.$$

¹Kapitza's method was used in quantum mechanics in the article by Popov, Kuznetsov, and Perelomov [14].

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The Stark effect is the shifting and splitting of spectral lines of atoms and molecules due to the presence of an external electric field. It is the electric-field analogue of the Zeeman effect, where a spectral line is split into several components due to the presence of the magnetic field. Although initially coined for the static case, it is also used in the wider context to describe the effect of time-dependent electric fields. In particular, the Stark effect is responsible for the pressure broadening of spectral lines. Real molecules are not always well-approximated as harmonic oscillators (particularly at larger separations, near the bond-breaking limits). Thus, the harmonic potential description of a diatomic does not take into consideration states close to dissociation. The Morse potential (Figure 19.6, Engel and Reid) shows a description of a potential that is anharmonic about the equilibrium nuclear separation, R_e . This is formally denoted as