

PLANNING OF NONCLASSICAL VIBRATIONAL STATES*

S. SZABÓ, ZS. KIS, J. JANSZKY, P. ADAM

*Research Laboratory for Crystal Physics, Hungarian Academy of Sciences
P. O. Box 132, H-1502 Budapest, Hungary*

T. KOBAYASHI

*Department of Physics, Faculty of Science, University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan*

AN. V. VINOGRADOV

*P. N. Lebedev Physical Institute
117924 Moscow, Russia*

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Methods are analyzed to find the pulse shape and chirp of the exciting light pulse to generate a given vibrational state of a molecule during Franck–Condon transitions. An example is given for generation of vibrational Schroedinger-cat states. Their remarkable feature is that they have simultaneously two distinguishable distances of the atoms in a diatomic molecule due to quantum mechanical superposition.

1. Introduction

A wide interest was addressed to wave packet formation and motion during Franck–Condon transitions in both theoretical and experimental points of view [1–4]. The nonclassical features of the emerging vibrational wave packets predicted in [1] have been experimentally found in [5].

The wave packet formation of the vibrational state is directly connected to the problem of one-dimensional representation [6, 7] of quantum states through the quasiclassical (coherent) states. It was shown [6–11] how the quantum interference between the coherent states involved in the superposition leads to the occurrence of non-classical features.

In this paper we shall discuss the possibilities to plan the shape and phase properties of the exciting laser pulse to achieve a given vibrational state after the electro-vibrational transition in molecules. As we shall see special states with rather peculiar properties can be created by appropriately chirped pulses with comparatively long duration.

* Dedicated to Professor István Kovács on his eightieth birthday

2. Franck–Condon transition

Let us consider the problem of a Franck–Condon transition in a diatomic molecule induced by a short coherent light pulse. The adiabatic model Hamiltonians of a two-level one-mode electro-vibrational system we use have the following second quantized forms in terms of the annihilation phonon operators b associated with the vibrational potential of the excited states (i and e denote the initial and excited electronic levels respectively)

$$\hat{q} = \sqrt{\frac{\hbar}{2M\omega}}(b^\dagger + b), \quad \hat{p} = i\sqrt{\frac{\hbar M\omega}{2}}(b^\dagger - b), \quad (1)$$

$$H_i = \epsilon_i + \frac{M\omega^2}{2}q_i^2 + \frac{1}{2}\hbar\omega(b^\dagger b + bb^\dagger) + \hbar\omega q_i \sqrt{\frac{M\omega}{2\hbar}}(b^\dagger + b), \quad (2)$$

$$H_e = \epsilon_e + \frac{1}{2}\hbar\omega(b^\dagger b + bb^\dagger), \quad (3)$$

where \hat{q} and \hat{p} are the coordinate and momentum operators. For the sake of simplicity it is supposed that due to the electronic transition $i \rightarrow e$ there is only shift (q_i) in the harmonic vibrational potential and no frequency change. The Hamiltonian of the initial state can be diagonalized by the unitary operator

$$\hat{\Delta} = e^{-g(b^\dagger - b)}, \quad (4)$$

$$g = q_i \sqrt{\frac{M\omega}{2\hbar}}.$$

Here g is the displacement parameter. The vibrational ground state of the initial electronic level is

$$|0\rangle_i = \hat{\Delta}|0\rangle_e, \quad (5)$$

where $|0\rangle_e$ is the vibrational ground state of the excited electronic level.

The Hamiltonian $H'(t)$ describing the interaction with the external field has the form

$$H'(t) = \frac{1}{2}d_{ie}E(t)a_e^\dagger a_i + \frac{1}{2}d_{ie}^*E^*(t)a_i^\dagger a_e, \quad (6)$$

where

$$E(t) = e(t) \exp(-i\Omega_0 t), \quad (7)$$

$a_{i(e)}$ is the annihilation operator of the $i(e)$ -th electron level, d_{ie} the dipole matrix element of the electronic transition, $|e(t)|^2$ and Ω_0 are the envelope function and the central frequency of the exciting pulse. Let $|i\rangle$ and $|e\rangle$ be the ground and excited electronic states of the molecule. Assuming that initially, at $t = -\infty$, the system is in the ground state $|i\rangle_i$, after the exciting pulse has passed the electronic–vibrational

wave function takes the following form according to the first order perturbation theory:

$$|\Psi, t\rangle = |i, t\rangle|0\rangle_i - i \frac{E_0 d_{ie}}{2\hbar} |e, t\rangle |\{E(t)\}\rangle_e. \tag{8}$$

Here $|\{E(t)\}\rangle_e$ is unnormalized vibrational wave function of the molecule of the excited electronic state in the interaction picture:

$$|\{E(t)\}\rangle_e = \int_{-\infty}^{\infty} d\tau \exp(i\delta\tau) e(\tau) |\alpha(\tau)\rangle_{coh}, \tag{9}$$

where δ is the difference between the zero phonon line and the exciting pulse central frequencies, $|\beta\rangle_{coh}$ is a coherent state with respect to the phonon operator $b(b|\beta\rangle_{coh} = \beta|\beta\rangle_{coh})$ and $\alpha(\tau) = ge^{-i\omega\tau}$. The expression $\{E(t)\}$ inside the ket-vector $|\{E(t)\}\rangle_e$ shows that the state depends on $E(t)$ as a functional.

For further considerations it is convenient to rescale the vibrational wave function by substituting $\phi = \omega\tau$ as follows

$$|\{E(t)\}\rangle_e \equiv |f\rangle = \frac{1}{\omega} \int_{-\infty}^{\infty} f(\phi) |re^{i\phi}\rangle d\phi, \tag{10}$$

$$f(\phi) = \exp\left(\frac{i\delta\phi}{\omega}\right) e\left(\frac{\phi}{\omega}\right).$$

The coherent states $|re^{i\phi}\rangle$ and $|re^{i(\phi+k2\pi)}\rangle$ $k = \pm 1, \pm 2 \dots$ are identical, therefore we can rearrange the pulse function $f(\phi)$ in the following form

$$h(\phi) = \sum_{k=-\infty}^{\infty} f(\phi + 2k\pi). \tag{11}$$

Shifting the index k is equivalent to shifting the argument with 2π therefore $h(\phi)$ is periodical. It can be readily seen that this function has the following property

$$\int_{-\infty}^{\infty} f(\phi) |re^{i\phi}\rangle d\phi = \int_{-\pi}^{\pi} h(\phi) |re^{i\phi}\rangle d\phi. \tag{12}$$

The right side of Eq. (12) describes a state that is superposition of coherent states of the same amplitude r . All these coherent states are on the same circle on the phase-space called α -plane. The weight and phase of a given coherent state in the superposition is determined by the distribution function $h(\phi)$. These circle superpositions form a whole one-dimensional representation [6, 7] and for a given state one can find the corresponding $h(\phi)$. If we can find an experimentally easily realizable pulse function $f(\phi)$ leading to the aimed $h(\phi)$, one can design the quantum state itself.

The distribution function $h(\phi)$ has the following form, considering that a periodical function is in question:

$$h(\phi) = \sum_{k=-\infty}^{\infty} h_k e^{ik\phi}. \quad (13)$$

It corresponds to the following Fock state expansion

$$|\psi\rangle = c_0 2\pi \sum_{k=0}^{\infty} \frac{h_{-k} g^k}{\sqrt{k!}} |n\rangle. \quad (14)$$

The terms h_k for $k > 0$ give no contribution to the state $|\phi\rangle$,

$$|\psi[h]\rangle = |\psi[h_0]\rangle, \quad h_0(\phi) = h(\phi) + \sum_{k=1}^{\infty} \tilde{h}_k e^{ik\phi}, \quad (15)$$

where \tilde{h}_k are arbitrary constants. It means that the distribution functions $h_0(\phi)$ and $h(\phi)$ lead to the same state. This fact can be used e.g. to eliminate complexity from $h(\phi)$ (if h_0 is real, then selecting $h_k = h_{-k}^*$ for $k > 0$), or with proper selection we can keep $|h(\phi)|$ well over zero. If the state $|\psi\rangle$ is given in form of Fock coefficients, we can easily calculate the corresponding function $h(\phi)$. The very question is how to design the proper light pulse to induce the required state, i.e. how to find a suitable pulse to build up a required vibrational state.

3. Envelope function method

In this Section we define a general and simple unwrapping method to find the pulse function $f(\phi)$ supposing that the distribution function $h(\phi)$ is given. Let us select an arbitrary function $g(\phi)$ for that

$$\int_{-\infty}^{\infty} g(\phi) < \infty. \quad (16)$$

Now we give a formula for $f(\phi)$ that fulfils Eq. (11)

$$f(\phi) = \frac{1}{\int_{-\infty}^{\infty} g(y) dy} \left(\int_{\phi-\pi}^{\phi+\pi} g(y) dy \right) h(\phi) = \text{env}(\phi) h(\phi). \quad (17)$$

The factor containing the integration formula can be considered as a special envelope function. It can be easily shown that this formula is correct. By summing up both sides of the equation and considering that $h(\phi)$ is periodical we obtain

$$h(\phi) = \sum_{k=-\infty}^{\infty} f(\phi + n2\pi) = \frac{\int_{-\infty}^{\infty} g(y) dy}{\int_{-\infty}^{\infty} g(y) dy} h(\phi) = h(\phi). \quad (18)$$

From the definition above it becomes clear that several functions $g(\phi)$ result in the same $env(\phi)$. Any modifying function $m(y)$ can be added to $g(y)$ keeping $env(\phi)$ invariant if $\int_{\phi-\pi}^{\phi+\pi} m(y)dy = 0$

$$env(\phi) = \frac{\int_{\phi-\pi}^{\phi+\pi} g(y)dy + 0}{\int_{-\infty}^{\infty} g(y)dy + 0} = \frac{\int_{\phi-\pi}^{\phi+\pi} g(y) + m(y)dy}{\int_{-\infty}^{\infty} g(y) + m(y)dy}. \tag{19}$$

If $h(\phi)$ is smooth itself then it can be unwrapped by a simple function $g(y)$ to get a smooth and experimentally easy to realize $f(\phi)$. Let us choose a simple function, for example $g(y) = e^{-a|y|}$ then

$$env(\phi) = \frac{1}{\rho} \int_{\phi-\pi}^{\phi+\pi} g(y)dy = \begin{cases} 1 - e^{-a\pi} ch(a\phi), & \phi \in [-\pi, \pi], \\ e^{-a|\phi|} sh(a\pi), & \text{otherwise,} \end{cases} \tag{20}$$

where we denote $\int_{-\infty}^{\infty} g(y)dy$ by ρ .

If $h(\phi)$ contains glitches then multiplying by a smooth envelope function the unwrapped function will keep the same hard to realize character though a complicated generating function $g(y)$ can unwrap a glitchy distribution function into a smooth pulse function $f(\phi)$.

As an example we find the generating function that is able to unwrap the glitchy distribution function

$$h(\phi) = \sum_{k=-\infty}^{\infty} e^{-\beta(\phi+2k\pi)^2} \tag{21}$$

to the corresponding smooth pulse function from which it was wrapped

$$f(\phi) = e^{-\beta\phi^2}. \tag{22}$$

We start from the basic definition of the unwrapping

$$f(\phi) = \frac{1}{\rho} \left(\int_{\phi-\pi}^{\phi+\pi} g(y)dy \right) h(\phi). \tag{23}$$

Dividing the equation by $h(\phi)$ and differentiating both sides of the equation by ϕ in first order

$$\frac{g(\phi + \pi) - g(\phi - \pi)}{\rho} = \frac{f(\phi)'h(\phi) - h(\phi)'f(\phi)}{h(\phi)^2} = S(\phi). \tag{24}$$

Using Eqs (21–22) we obtain

$$S(\phi) = 4\pi\beta \frac{f(\phi) \sum_{k=-\infty}^{\infty} k f(\phi + 2k\pi)}{h(\phi)^2}. \tag{25}$$

We can assume $\lim_{\phi \rightarrow \infty} g(\phi) = 0$ therefore the recursion

$$\frac{g(\phi)}{\rho} = \frac{g(\phi - 2\pi)}{\rho} + S(\phi - \pi) \quad (26)$$

can be continued and finally the term $\frac{g(\phi - 2k\pi)}{\rho}$ vanishes. So we get

$$\begin{aligned} \frac{g(\phi)}{\rho} &= \sum_{k=0}^{\infty} S(\phi - (2k + 1)\pi) = \\ &= 4\pi\beta \frac{\sum_{l=0}^{\infty} f(\phi - (2l + 1)\pi) \sum_{k=-\infty}^{\infty} k f(\phi + (2k - 2l - 1)\pi)}{h(\phi - \pi)^2}. \end{aligned} \quad (27)$$

4. Unwrapping to a Gaussian function

In the previous Section we saw that a whole class of pulse functions can result in the same distribution function $h(\phi)$, the unwrapping process is not unambiguous. Via the former process we can get complex $f(\phi)$ functions with simply behaving phase (supposing $h(\phi)$ has such one) and inconvenient amplitude properties. In this Section we will search for $f(\phi)$ in the following form

$$f(\phi) = C e^{-u\phi^2 + iA(\phi)}, \quad (28)$$

where C is an unknown real constant and $A(\phi)$ an unknown real function. We consider u given. This case corresponds to a Gaussian exciting laser pulse laser with complicated chirping behaviour.

First we analyze in detail what happens on the complex number plane \mathbb{C} when we execute the wrapping. Function $h(\phi)$ is a periodical complex function, therefore we have a closed curve on the plane \mathbb{C} . For a given argument of $h(\phi)$ it is built by infinite small vectors (the elements of the sum in Eq. (11)). Let us denote the full length of the elementary vectors by $L_0(\phi)$

$$L_0(\phi) = \sum_{k=-\infty}^{\infty} e^{-u(\phi + 2k\pi)^2}. \quad (29)$$

Giving $A(\phi)$ means we describe how to direct the elementary vectors of \mathbb{C} , how to bend the curve. If we choose C too small then we cannot reach the curve of $h(\phi)$ even by a straight superposition, therefore our first condition will be

$$CL_0(\phi) - |h(\phi)| \geq 0. \quad (30)$$

It gives a lower limit for C . We choose C

$$C = \min \left(\frac{|h(\phi)|}{L_0(\phi)} \right). \quad (31)$$

We denote the angle fulfilling this condition by ϕ_0 and we select it in the domain $[-\pi, \pi]$. If there are more than one an arbitrary one can be selected of them. For $\phi = \phi_0 + 2k\pi$ all the vectors have the same direction,

$$A(\phi_0) = A(\phi_0 + 2k\pi) = \arg(h(\phi_0)). \tag{32}$$

For $\phi \neq \phi_0 + 2k\pi$ the full length of the elementary vectors is longer than $|h(\phi_0)|$. For simplicity we broke the curve into two straight segments. It means for a given ϕ all the elementary vectors use two phase angles

$$A(\phi) = \begin{cases} A_1(\phi) & \text{for } \phi < \phi_0, \\ A_2(\phi) & \text{for } \phi > \phi_0, \end{cases} \tag{33}$$

where $A_1(\phi)$ and $A_2(\phi)$ are 2π periodic functions. First we calculate the lengths of the two constituting segments

$$L_1(\phi) = \begin{cases} \sum_{k=0}^{k=\infty} C e^{-u(\phi-2k\pi)^2} & \text{for } \phi < \phi_0, \\ \sum_{k=1}^{k=\infty} C e^{-u(\phi-2k\pi)^2} & \text{for } \phi > \phi_0, \end{cases}$$

$$L_2(\phi) = \begin{cases} \sum_{k=1}^{k=\infty} C e^{-u(\phi+2k\pi)^2} & \text{for } \phi < \phi_0, \\ \sum_{k=0}^{k=\infty} C e^{-u(\phi+2k\pi)^2} & \text{for } \phi > \phi_0. \end{cases} \tag{34}$$

Now the angles $A_1(\phi)$ and $A_2(\phi)$ can be calculated by the sine and cosine theorem by introducing two functions

$$\alpha_1(\phi) = \arccos \left(\frac{L_1(\phi)^2 + L_2(\phi)^2 - |h(\phi)|^2}{2L_1(\phi)L_2(\phi)} \right) \tag{35}$$

and

$$\alpha_2(\phi) = \arcsin \left(\frac{L_2(\phi)}{|h(\phi)|} \sin(\alpha_1(\phi)) \right). \tag{36}$$

From here

$$A_1(\phi) = \arg(h(\phi)) \pm \alpha_2(\phi) \tag{37}$$

and

$$A_2(\phi) = A_1(\phi) - \pi \pm \alpha_1(\phi) = \arg(h(\phi)) \pm (\alpha_1(\phi) + \alpha_2(\phi)) - \pi. \tag{38}$$

This process in some cases cannot be used. If we break the curve into two segments then not only maximal distance condition (Eq. (30)) exists but also one for the minimal distance because of the cosine theorem

$$|h(\phi)| > |L_1(\phi) - L_2(\phi)|. \tag{39}$$

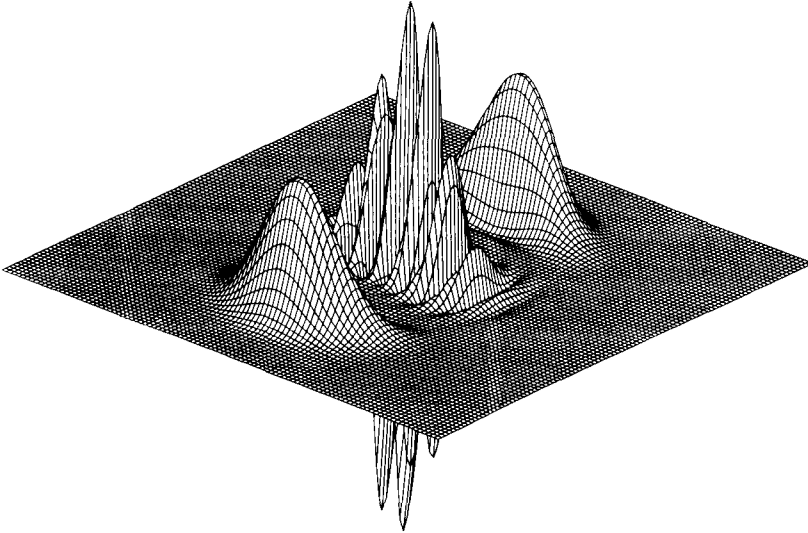


Fig. 1. The Wigner function of the vibrational state created by a relatively long, linearly chirped light pulse during a Franck–Condon transition. The chirp was chosen to match the pulse duration so that a two-peaked distribution function could lead to a vibrational Schroedinger-cat state. The fringes in the middle of the picture are originated form the quantum mechanical interference.

In this case the curve may be broken into three or more parts. A too large parameter u can result in one very long segment comparing to the others, and in this case no $A(\phi)$ can be found.

As a physical example we consider a vibrational state with two-peaked distribution function $h(\phi)$ which has an unwrapped pulse function $f(\phi)$ of form of Eq. (28) with quadratic $A(\phi)$ function. This corresponds to a long linearly chirped exciting pulse function $e(t)$. In Fig. 1 we show the final Wigner function of the resulting vibrational state. The Wigner function is a function of a complex variable α . An integral of the Wigner function by the imaginary axis of the α -plane yields the absolute square of the wave function in q -representation, i.e. $|\Psi(q)|^2$. Due to the quantum mechanical interference a fringe pattern appears between the Gaussian-like bells representing the two parts of the superposition states in the Wigner function picture. This fringe pattern is transformed characteristically when the positions or the phase of the involved coherent states change.

In Fig. 2 the time evolution of the unnormalized wave function of a state is shown during the excitation by such a chirped pulse

$$\langle q|\{E(t)\}, t\rangle_e = \int_{-\infty}^t d\tau \exp(i\delta\tau) \exp\left(-\frac{u^2}{2}t^2 + i\frac{\omega^2}{2}t^2\right) \langle q|\alpha(\tau)\rangle_{coh}, \quad (40)$$

with reciprocal pulse duration $u = 0.1$, chirp $w = 0.546\omega$ and parameters $g = 3\omega$

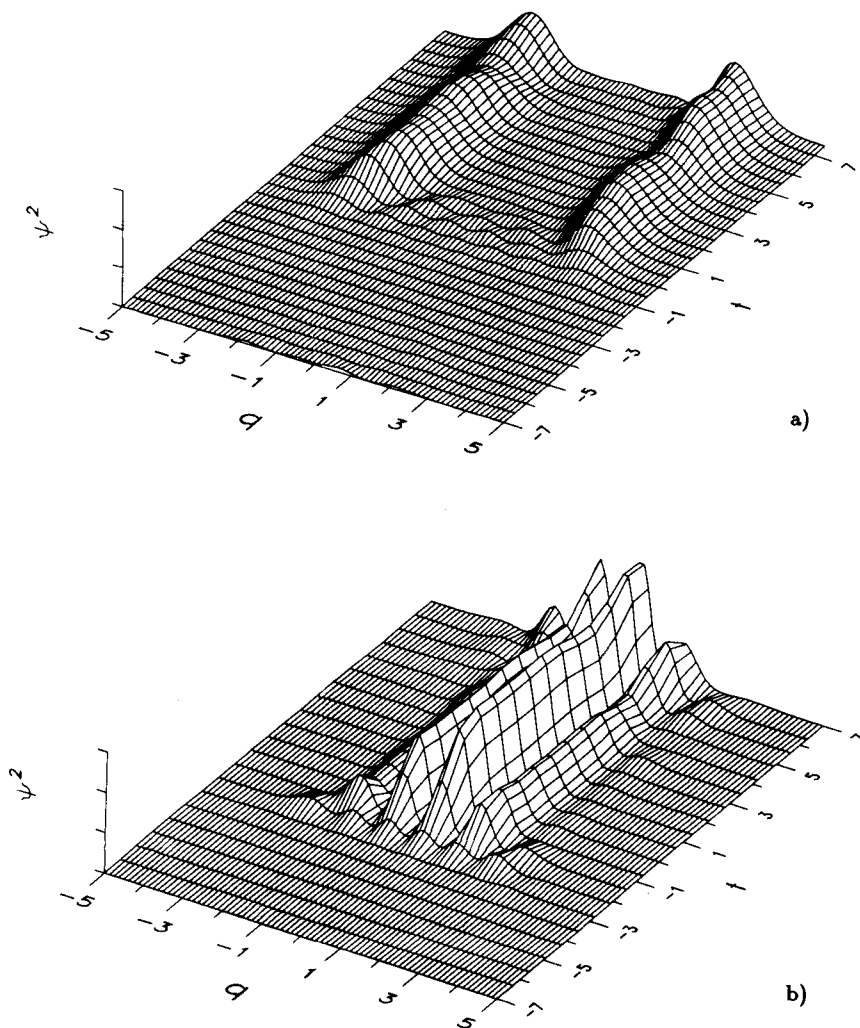


Fig. 2. The time evolution of the absolute square of the unnormalized vibrational state in coordinate-representation during a Franck-Condon transition due to a specially chosen chirped exciting pulse a) at times $t = \pm m \frac{T}{2}$; b) at times $t = \pm m \frac{T}{2} + \frac{T}{4}$, $m = 1, 2, \dots$. The time is shown in the units of the vibrational period T . One can see that as the pulse passes the state evolves into a Schrödinger-cat state with well defined double distance between the atoms at the turning points of the vibration (Fig. 2a)

and $\delta = 9\omega$. We can see that by a chirped pulse one can excite the vibrational state during a Franck-Condon transition into a rather peculiar state with two well-distinguishable distances between the same atoms of the molecule at the same mo-

ments of time. Such state is a complete analog of the widely discussed optical Schroedinger-cat states [1, 8–11]. Moreover, these two distances may enable one to create chemical Schroedinger-cat states by some process depending on the distance between the atoms in the molecule [12].

5. Conclusion

In the Franck–Condon transition introduced by a short light pulse different pulses with different electric field strengths $E(t)$ can lead to the same vibrational $|\Psi\rangle$ of the excited electronic level. We have given two different methods making possible designing a pulse function $E(t)$ that excites the desired vibrational state. The first method uses an envelope function that cuts off the periodical distribution function $h(\phi)$ in $\pm\infty$. This method can be used in any case, and via the possibility of choosing an arbitrary generating function, a wide range of possible $E(t)$ results. The other method uses a fixed Gaussian envelope function, and the amplitude as well as the phase behaviour of the complex $E(t)$ function are found. In some cases this latter procedure may fail, but usually results in experimentally more easily realizable $E(t)$. We used the vibrational Schroedinger-cat state as an example to demonstrate the operation of these techniques.

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