

A Solid-State Model for Photonic Localization in Molecular Quasi-Continua.

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Abstract. - Coherence effects in the excitation of molecules by a monochromatic field in a quasi-continuum of states are investigated and shown to give rise to localization of the excitation energy. Our results follow from a simple model derived from the underlying Hamiltonian and containing the essential physics.

Multiphoton excitation of large molecules in the collisionless regime is a problem of long-standing interest with important practical applications [1, 2]. The question has repeatedly been discussed whether a rate equation approach is sufficient or coherence effects might play a role in the transport up the energy ladder from the distinctly discrete levels at the bottom through an intermediate quasi-continuum of states into the continuum [3, 4]. It seems clear that coherence effects are important near the bottom, but it has often been argued that a rate equation approach is sufficient in the quasi-continuum and the continuum. Akulin and Dykhne [5] derived a model from the underlying Hamiltonian and obtained the diffusion rate of the excitation energy in the quasi-continuum. Meanwhile the extensive study of quantum models like the kicked rotator [6], the Morse map [7], the Kepler map and the one-dimensional hydrogen atom in an external high-frequency field [8] and experimental studies of hydrogen atoms in microwave fields [9] have established the existence of a quantum-mechanical coherence effect, «photonic» localization, which could have a strong influence on the excitation of molecules by a monochromatic external field in the quasi-continuum.

In the present paper we wish to analyse this problem. We first reduce the Schrödinger equation to the Akulin-Dykhne model [5] and then incorporate the further assumption that the matrix elements for the excitation vary smoothly throughout the quasi-continuum and can be replaced by a constant. We find that in this case the problem can be mapped on a simple 1-dimensional solid-state model with nearest-neighbour interaction and diagonal disorder stemming from randomness in the level spacings of the molecule and incommensur-

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ability of the mean level spacing with the externally applied frequency. Without randomness the model is exactly solvable and we obtain continuous bands of quasi-energies corresponding to delocalized Bloch states. With randomness Anderson localization occurs and the localization length is easily computed. Under conditions where the molecular levels have some rigidity, we find a systematic dependence of the localization length on the quasi-energies. It is large and proportional to the square of the matrix element for quasi-energies near the former band centre, and smaller and proportional to the magnitude of the matrix element for quasi-energies in the former band gap.

We start from the Schrödinger equation (with $\hbar = 1$) for the probability amplitudes d_N of the unperturbed molecular states $|n\rangle$

$$i\dot{d}_n = E_n d_n + 2 \cos \omega t \sum_{n'} V_{nn'} d_{n'}, \quad (1)$$

where $E_n = n/\rho + \varepsilon_n$, ρ is the average density of states in the quasi-continuum which we shall normalize to $\rho = 1$, ε_n is random (see below), and $V_{nn'}$ is the product of the external field amplitude and the matrix element between the states $|n\rangle$, $|n'\rangle$. The external frequency ω is taken as $\omega \gg 1$, *i.e.* large compared to ρ^{-1} . Introducing $\tilde{d}_n(t) = \exp[-im_n \omega t] C_n(t)$, where $m_n = [E_n/\omega]$ is the integer closest to E_n/ω , and making the «rotating wave» approximation, *i.e.* neglecting oscillatory terms, which to a good approximation are averaged out on the remaining longer time scale, we obtain the Akulin-Dykhne model

$$i\dot{C}_n = \omega \delta_n C_n + \sum_{n'} V_{nn'} (\delta_{m_n, m_{n'+1}} + \delta_{m_n, m_{n'-1}}) C_{n'}, \quad (2)$$

with $\omega \delta_n = E_n - m_n \omega$, $|\delta_n| \leq 1/2$.

Equation (2) implies that 1-photon transitions occur only between neighbouring groups of molecular eigenstates of the size of one photon energy. In the following we shall assume that $V_{nn'}$ changes on a scale larger than ω and approximate $V_{nn'} = V$. With $C_n = a_n^{(\lambda)} \exp[-i\omega_\lambda t]$, where the ω_λ are quasi-energies and defined for $-\omega/2 < \omega_\lambda \leq \omega/2$, and

$$K_m^{(\lambda)} = \sum_n a_n^{(\lambda)} \delta_{m, m_n}, \quad (3)$$

we can rewrite eq. (2) as

$$a_n^{(\lambda)} = \frac{V}{\omega_\lambda - \omega \delta_n} (K_{m_n+1}^{(\lambda)} + K_{m_n-1}^{(\lambda)}). \quad (4)$$

Defining the generally random function $(F_m(\omega_\lambda))^{-1} = \sum_n \delta_{m, m_n} / (\omega_\lambda - \omega \delta_n)$, we arrive at

$$F_m(\omega_\lambda) K_m^{(\lambda)} = V(K_{m+1}^{(\lambda)} + K_{m-1}^{(\lambda)}), \quad (5)$$

which can be viewed as a solid-state model with nearest-neighbour interaction and diagonal disorder. The eigenfunctions $K_m^{(\lambda)}$ of this model will be localized. Note that the «site-index» m counts the member of the photons, and the localization length therefore is measured in the number of photons. Once the eigenfunctions $K_m^{(\lambda)}$ have been determined, the amplitudes $a_n^{(\lambda)}$ follow from $a_n^{(\lambda)} = F_{m_n}(\omega_\lambda) K_{m_n}^{(\lambda)} / (\omega_\lambda - \omega \delta_n)$ and, in general, will have very large fluctuations, because the denominator can become small. States for different ω_λ will have quite different amplitudes within a block of given m_n , even if their amplitudes K_m are similar. In the

simplest case without randomness of the levels $\epsilon_n = 0$. If in addition the number of levels of the quasi-continuum is very large, it may be taken as infinite in the evaluation of the sum for $(F_m(\omega_\lambda))^{-1}$. Then we obtain

$$(F_m(\omega_\lambda))^{-1} = \pi \operatorname{ctg}(\pi(\omega_\lambda - \nu_m)) \tag{6}$$

with $\nu_m = m\omega$. For typical irrational values of ω the model is exactly solvable [10]. The spectrum of quasi-energies is pure point, and the eigenstates are localized. Even if the randomness caused by the ϵ_n is negligible within each block of the size of a photon it may still give rise to random values of ν_m . In that case, if the values of $\nu_m(\operatorname{mod} \omega)$ are randomly distributed in the interval ω , eq. (5) reduces to the analytically solved Lloyd model. As was shown in [11] the Lloyd model can be mapped exactly on the model for the kicked rotator with a potential proportional to arctg of the rotation angle, which therefore also describes our model for the present case. The localization length for the Lloyd model is known explicitly, and, for $\rho|V| \gg 1$ it is given by

$$l = 2\pi|V|. \tag{7}$$

In the case without randomness, if the frequency ω is an integer multiple of ρ^{-1} , *i.e.* an integer in our units, then all m -dependence disappears from eq. (6) and eq. (5) is solved by extended plane waves $\sim \exp[i2\pi km]$, $|k| < 1/2$, with the continuous band spectrum

$$\omega_\lambda(k) = \frac{1}{\pi} \operatorname{arctg}[2\pi V \cos 2\pi k] + \lambda, \quad -\frac{\omega}{2} < \lambda < \frac{\omega}{2}, \quad \omega \gg 1, \quad \lambda \text{ integer}, \tag{8}$$

i.e. the excitation propagates coherently through the quasi-continuum. The energies $\omega_\lambda(k)$ occur in bands of width $\Delta = (2/\pi) \operatorname{arctg}(2\pi V)$ with centres at integer values of ω_λ and gaps around half-integer values of ω_λ . For small V the bands appear just at the position of the unperturbed levels. In the case when the molecular levels have random positions, described by ϵ_n , $F_m(\omega_\lambda)$ is random and eq. (5) has to be solved numerically, which is an easy task, using

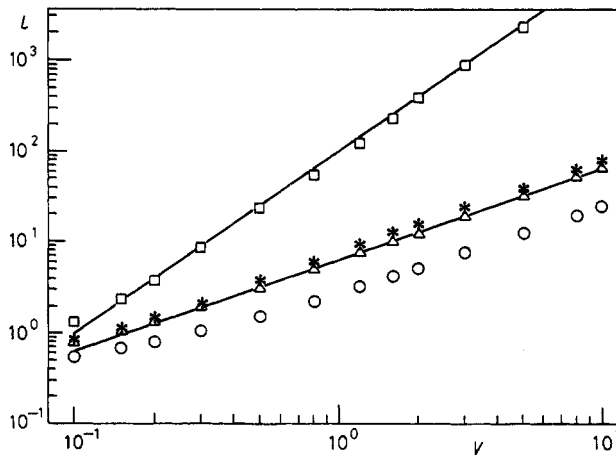


Fig. 1. - Localization l vs. the matrix element $|V|$ in a doubly logarithmic plot. Different symbols correspond to case i) with quasi-energies in the band centre (\square), in the gap (\circ), in the middle between gap and band centre ($*$), and case ii) (\triangle). The full lines give l_A for the Anderson model in the middle of the band, and l_L for the Lloyd model.

the transfer matrix technique [12]. Special checks were made that the number of states $\rho\omega$ within one photon interval, if sufficiently large, does not influence the final results. Usually we chose $\rho\omega = 128$. In fig. 1 we present results for the localization lengths as a function of the matrix element $|V|$ obtained under two different statistical assumptions on the ε_n :

i) The ε_n are assumed to be independently and homogeneously distributed in the unit interval $-1/2 < \varepsilon_n \leq 1/2$ and $\rho\omega$ is taken integer. In this case each energy level E_n is rigidly confined to $n - 1/2 < E_n \leq n + 1/2$. We find that the localization length depends systematically on the energies ω_λ , *i.e.* the band structure of the nonrandom system is not entirely washed out. For ω_λ close to the former band centres $\omega_\lambda \approx \lambda$ the localization length is large and proportional to $|V|^2$. This dependence is expected for Anderson localization in a weakly random 1-dimensional system with long mean-free path, which corresponds to a case with a small density of impurities [13]. For ω_λ outside the centres of the former bands the localization length is smaller and proportional to $|V|$ like in the Lloyd model.

ii) The levels E_n are distributed on the real line as a discrete Poisson process with independent random increments in the interval $(0, 2]$. In this case there is practically no dependence of the localization length on ω_λ . For all ω_λ the localization length is proportional to $|V|$ as in the Lloyd model, which also gives a good estimate of the prefactor. In the doubly logarithmic plot shown in fig. 1 we compare the results for the localization length for the different cases we have studied.

Let us also compare these results with some simple estimates. There is a general connection between the quantum-mechanical localization length l of quasi-energy eigenfunctions in the number of photons and the diffusion constant D of energy over one period, $l = (D/2\omega)$ [8, 12]. Assuming that the diffusion constant is determined via $D = 2\omega^2(2\gamma)(2\pi/\omega)$ by the 1-photon transition rate 2γ and calculating the latter from the Fermi golden rule one obtains $l_F = 4\pi^2|V|^2$. In strong external fields one may expect that the 1-photon transition rate saturates and Deng and Eberly [14] have shown how to take this effect into account. In our present case their method yields $2\gamma = |2V|^2/(2(\pi\rho)^{-1} + 2\gamma) \approx |2V|$ for $|2V| \gg 2(\pi\rho)^{-1}$. Under the same assumption as before we then find $l_{DE} = 4\pi|V|$. This result gives the same dependence on $|V|$ as the Lloyd model, $l_L = 2\pi|V|$, with a different prefactor, however. From the Anderson model in the limit of small randomness, one obtains [15] $l_A \approx 100|V|^2$, similar to the result obtained via the golden rule, but again with a different prefactor. Comparing these estimates with our results for case i) we can see that the results based on the 1-photon transition rates give the $|V|$ -dependence correctly away from the band centre if the saturation is taken into account. However, the prefactor differs roughly by a factor 2. The localization length at the band centre should not be compared with an estimate based on the transition rate, because these estimates [12] assume that the localization length is independent of ω_λ , at least approximately. The numerical results give the following dependence of the localization length on the matrix element V : in case i), in the middle of the gap $l \approx 2.5|V|$, in the band centre $l \approx 90|V|^2$, in the middle of the gap and the centre of the band $l \approx 8|V|$. The localization length at the band centre agrees well with l_A , while l_L gives the best estimate for the other cases. In case ii) $l \approx 7|V|$ without dependence on the quasi-energy. This case agrees well with the Lloyd model. The linear dependence of l on $|V|$ can be understood physically by saturation [14].

In conclusion we have shown that molecular excitation in a quasi-continuum by multi-photon absorption under some simplifying assumptions can be described by a solid-state model, which in some cases can be reduced even further to the Lloyd model. The molecule then absorbs energy from the external field like a quantized periodically kicked rotator, *i.e.* the complexity of the system is drastically reduced. Localization in the number of absorbed

photons occurs in the quasi-continuum with a localization length which, remarkably, is independent of the photon energy, and, depending on the case under consideration, can be estimated from the Anderson model or the Lloyd model, or, up to factors of order 1, from an extension of the golden rule including saturation effects.

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