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## FAST TRACK COMMUNICATION

# Laser-induced conical intersections in molecular optical lattices

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Online at [stacks.iop.org/JPhysB/41/221001](http://stacks.iop.org/JPhysB/41/221001)**Abstract**

Conical intersections of potential energy surfaces widely appear in molecules which consist of *more* than two atoms. No conical intersections exist in the case of *free* diatomic molecules. We show here that diatomic molecules interacting with standing laser waves produce periodic arrays of conical intersections. At these laser-induced intersections the non-adiabatic effects are infinitely strong. The translational and rovibrational molecular motions become strongly coupled to each other and energy exchange between the various degrees of freedom influences the dynamics of the system. As an illustrative example, an effect of the laser-induced conical intersections on trapping of ultracold diatomic molecules by light is discussed.

(Some figures in this article are in colour only in the electronic version)

Conical intersections (CIs) between electronic potential energy surfaces are ubiquitous in polyatomic molecular systems and play a crucial role in various processes, for reviews see e.g. [1–3]. For nuclear geometries in the vicinity of a conical intersection, the Born–Oppenheimer separation between the electronic and the nuclear degrees of freedom breaks down, and non-adiabatic coupling effects become fundamentally important. The CI induces fast energy exchange between the electronic and nuclear motions in polyatomic molecules and plays a key mechanistic role in the spectroscopy of polyatomic molecules, photochemistry and chemical kinetics. CIs are also observed in the completely different contexts of optical physics [4, 5] and superconductor physics [6].

Importantly, CIs in molecules can be formed only if the studied molecular system possesses at least two independent nuclear coordinates whose changes influence the electronic wavefunction. Obviously, there cannot be any CI for diatomic molecules in free space. It has been demonstrated that CIs can appear for diatomics in intense *static* magnetic fields [7, 8]. The magnetic fields needed to create these CIs are usually far too intense to be available in the laboratory.

In the present work, we show for the first time that by using laser light it is possible to create another conceptually different kind of CIs in diatomics. Specifically, we find that a diatom placed inside a standing laser field (optical lattice) leads to a periodic array of CIs induced by the laser field. Beyond being a fundamentally new laser–matter phenomenon, these light-induced CIs can influence the physics of diatoms in optical lattices. Explicitly, it is demonstrated below that the trapping efficiency of a diatomic molecule in its lowest electronic state can be significantly reduced due to the presence of the mentioned light-induced CIs.

Trapping and manipulating atoms and molecules in optical lattices has been the subject of intense research [9–13] and is emerging as a forefront field in atomic, molecular and optical physics, as well as in condensed matter physics. This spans the controllability of atomic/molecular degrees of freedom by laser fields on one hand, and the design and realization of quantum phases of matter in optical lattices [13] on the other hand. From the above perspective, the merit of our work is also to provide a new interdisciplinary bridge between two different and substantial fields: the ‘mature’ molecular-dynamics and ‘newer’ optical-lattice physics.

Before demonstrating theoretically the formation of CIs in optical lattices, let us emphasize that these new kinds of CIs are easily created and controlled by using lasers with intensities typically available in laboratories. These CIs are attributed exclusively to the presence of laser light, which couples the *translational* centre-of-mass motion with the *internal* rovibronic motions, and introduces in this way additional nuclear degrees of freedom required for the formation of CIs. CIs are known to have severe impact on the dynamics of the system, and in the present case this also applies to the translational motion.

The Hamiltonian of a diatomic molecule in a standing linearly polarized laser wave with the frequency  $\omega_L$  has been derived before [14, 15], and is given by formula

$$\mathbf{H}(t) = \hat{T}_{XYZ} + \hat{T}_{R,\theta,\phi} + \mathbf{H}_{el}(R) + \varepsilon_0 \cos(k_L Z) \cos(\omega_L t) \Sigma_j(z_j \cos \theta + x_j \sin \theta) \quad (1)$$

Here,  $\hat{T}_{XYZ}$  and  $\hat{T}_{R,\theta,\phi}$  are respectively the kinetic energy operators for the translational motion of the centre of mass of the molecule ( $X, Y, Z$ ) and for the rovibrational ( $R, \theta, \phi$ ) molecular motion.  $\varepsilon_0$  is the maximum laser field amplitude and  $k_L$  stands for the wave vector  $k_L = \omega_L/c$ .  $\mathbf{H}_{el}(R)$  is the electronic Hamiltonian and  $\{x_j, y_j, z_j\}$  are the body-fixed electronic coordinates (the  $z$ -axis coincides with the molecular axis).

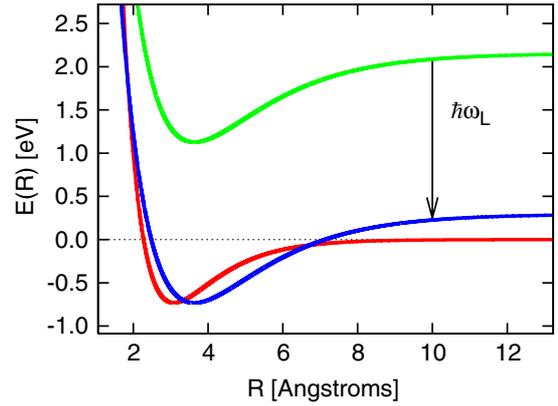
To further reduce the general Hamiltonian (1), we proceed in complete analogy to the routine procedure used to derive the Hamiltonian for atomic optical lattices [9, 16], and choose the laser frequency  $\omega_L$  to couple two electronic states  $|\psi_1^{\text{elec}}\rangle$  and  $|\psi_2^{\text{elec}}\rangle$  of the molecule by single photon excitation. For demonstration we choose the specific example of  $\text{Na}_2$  where the  $X^1\Sigma_g^+$  and  $A^1\Sigma_g^+$  electronic states are coupled by laser wavelength  $\lambda = 667$  nm. Due to symmetry, the only non-vanishing dipole matrix element responsible for light-induced electronic transitions is  $d(R) = \langle \psi_1^{\text{elec}} | \Sigma_j z_j | \psi_2^{\text{elec}} \rangle$ . In the space of the two electronic states, the Hamiltonian (1) reduces to the following  $2 \times 2$  matrix Hamiltonian,

$$\hat{H} = [\hat{T}_{XYZ} + \hat{T}_{R,\theta,\phi}] \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \times \begin{pmatrix} E_1(R) - \hbar\omega_L & \varepsilon_0 \cos \theta \cos(k_L Z) d(R)/2 \\ \varepsilon_0 \cos \theta \cos(k_L Z) d(R)/2 & E_0(R) \end{pmatrix}; \quad (2)$$

where  $E_0(R)$  and  $E_1(R)$  are the electronic energies. This Hamiltonian governs the motion of the centre of mass and of the vibrations and rotations of the diatomic molecule in standing laser field in the space of the two electronic states. The molecular Hamiltonian (2) ‘boils down’ to the well-known expression for the Hamiltonian of atoms in standing laser waves (see, e.g., equation (A.2) in [16]) if the nuclear coordinates ( $R, \theta, \phi$ ) are put to zero. Then, the energies  $E_0$  and  $E_1$  and the dipole matrix element  $d$  are constants and, of course, the rovibrational kinetic energy operator vanishes.

Let us show now that the effective Hamiltonian (2) gives rise to laser-induced CIs. As usual, we diagonalize the potential matrix in (2) (last term) and obtain the two Born–Oppenheimer potential energy surfaces  $V_{\pm}^{\text{ad}}(Z, R, \theta)$ . These surfaces exhibit an intersection only if the two conditions

$$\cos \theta \cos(k_L Z) = 0 \quad (3)$$



**Figure 1.** Potential energy curves  $E_0(R)$  and  $E_1(R)$  associated with the  $X^1\Sigma_g^+$  and  $A^1\Sigma_g^+$  electronic states of  $\text{Na}_2$ . Also shown is the shifted curve  $E_1(R) - \hbar\omega_L$  exhibiting crossings which satisfy condition (4) for conical intersections induced by a standing laser wave.

and

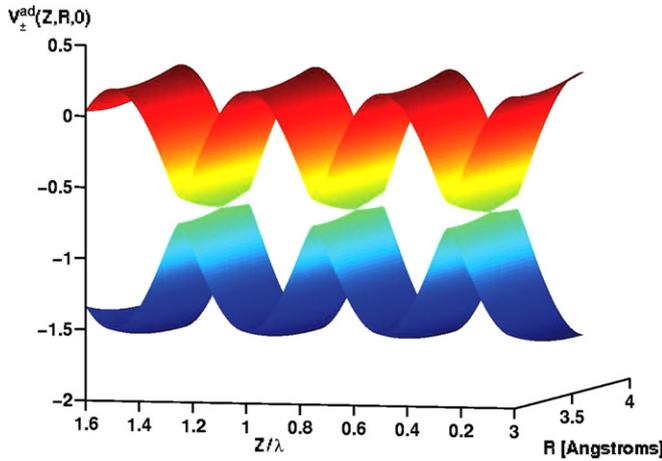
$$E_1(R) - E_0(R) = \hbar\omega_L \quad (4)$$

are simultaneously fulfilled. At the intersection the coupling term in the potential matrix of  $\hat{H}$  in (2) vanishes and the diagonal elements are degenerate.

The first condition (3) can be met either by setting  $\theta = (\pi/2)$  for arbitrary  $Z$ , or by setting  $Z = Z_n = (n + (1/2))(\pi/k_L)$ , ( $n$  integer), while  $\theta$  is arbitrary. The second condition (4) where the two electronic energy curves cross is naturally fulfilled by choosing the laser frequency to be in the vicinity of the electronic transition used to produce the optical lattice. Around each of the resulting intersections, the two surfaces exhibit the topology of a CI [1–3]. The slopes of these CIs along the  $Z$  and the  $\theta$ -directions are linearly proportional to the laser field intensity. More precisely, there are two branches of CIs, one in the  $(R, Z)$ -plane (for arbitrary values of  $\theta$  ( $\theta \neq \pi/2$ )), and one in the  $(R, \theta)$ -plane (for arbitrary values of  $Z$ ,  $Z \neq Z_n$ ). The overall topology is that of a *biconical* intersection [17]. We have thus shown that CIs can be generated in molecular systems (even in diatomics) by lasers. The laser induces a non-separability between the molecular centre-of-mass motion and the internal motions. This mechanism for generating CIs has not been proposed before, and may lead to new experiments and new phenomena.

We return to the sodium dimer. In figure 1 we display the energies  $E_{0,1}(R)$  and the shifted curve  $E_1(R) - \hbar\omega_L$  of the  $X^1\Sigma_g^+$  and  $A^1\Sigma_g^+$  electronic states. These energies and the dipole function  $d(R)$  are taken from [18]. The adiabatic surfaces  $V_{\pm}^{\text{ad}}(Z, R, \theta)$  which are the eigenvalues of the potential matrix (last term in equation (2)) are plotted in figure 2 for  $\theta = 0$ . A similar picture is also obtained when the angle  $\theta$  is allowed to vary while the coordinate  $Z$  is held fixed at a constant value  $Z \neq Z_n$ . It is seen that the CIs are generated periodically in nuclear coordinate space due to the spatial periodicity of the standing laser wave.

Let us illustrate how the presence of laser-induced CIs leads to a breakdown of the Born–Oppenheimer picture of single surface quantum dynamics. To this end it is useful to



**Figure 2.** The two adiabatic potential energy surfaces  $V_{\pm}^{ad}(Z, R, 0)$  of  $\text{Na}_2$  exhibiting a periodic array of CI points. We zoom here into the range related to the lower crossing point in figure 1. The laser wavelength is  $\lambda = 667$  nm. For illustrational reasons, in order to better visualize the topology of the conical intersections, the calculation has been done using a high laser intensity  $I = 3 \times 10^{13} \text{ W cm}^{-2}$ . Note, however, that CIs do exist here for *any* nonzero laser field strength. Note also that in our calculations on the consequences of CIs discussed below (see figure 4), a very weak laser field has been used. The profile of the cut of the CIs along the  $R$ -axis where  $\cos(k_L Z_n) = 0$  is exactly the same as the shape of the two potentials which are crossed in figure 1 (marked by an arrow).

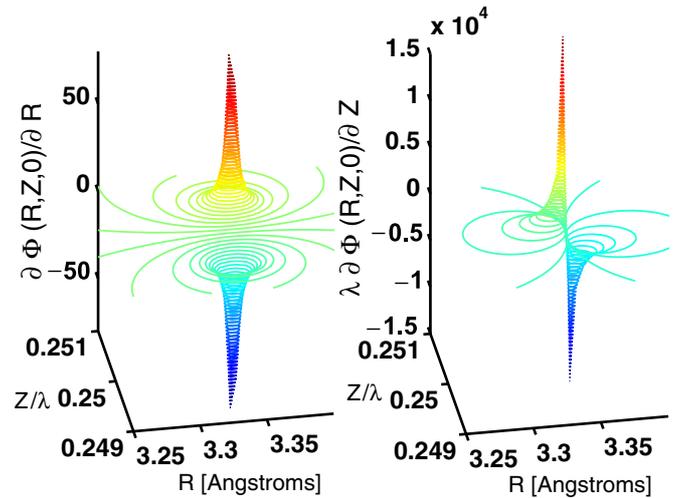
introduce the unitary matrix  $\hat{U}$  which diagonalizes the potential matrix of  $\hat{H}$  in (2) and thus transforms  $\hat{H}$  to the adiabatic representation:

$$\hat{U}(Z, R, \theta) = \begin{pmatrix} \cos \Phi(Z, R, \theta) & \sin \Phi(Z, R, \theta) \\ -\sin \Phi(Z, R, \theta) & \cos \Phi(Z, R, \theta) \end{pmatrix}, \quad (5)$$

where

$$\Phi(Z, R, \theta) = \frac{1}{2} \arctan \left( \frac{\varepsilon_0 \cos \theta \cos(k_L Z) d(R)}{E_1(R) - \hbar \omega_L - E_0(R)} \right). \quad (6)$$

In this representation  $\hat{U} \hat{H} \hat{U}^\dagger$  exhibits the adiabatic potential surfaces  $V_{\pm}^{ad}(Z, R, \theta)$  discussed above along its diagonal, but the kinetic energy operator now contains non-adiabatic couplings [1–3] of the form  $g_R(Z, R, \theta)(\partial/\partial R)$ , and analogously for  $Z$  and  $\theta$ . Using equations (5) and (6) it is easy to see that the functions  $g$  can be expressed in terms of the derivatives of the transformation angle  $\Phi$  with respect to the corresponding nuclear coordinate. In figure 3 we show the profiles of  $\partial\Phi(Z, R, \theta = 0)/\partial R$  and  $\partial\Phi(Z, R, \theta = 0)/\partial Z$  calculated in the vicinity of a CI. Similarly to the case of the common CIs encountered in polyatomic molecules, we encounter strong non-adiabatic couplings around each CI point which become singular at these points. The derivative  $\partial\Phi(Z, R, \theta)/\partial\theta$  not shown here possesses a similar singular behaviour. In summary, we may conclude that the light-induced CIs introduce infinitely strong non-adiabatic couplings. The Born–Oppenheimer picture breaks down and, in general, the nuclear dynamics proceeds on the coupled potential surfaces and the motions along the various coordinates, translation  $Z$ , vibration  $R$  and molecular rotation  $\theta$ , become intricately coupled.



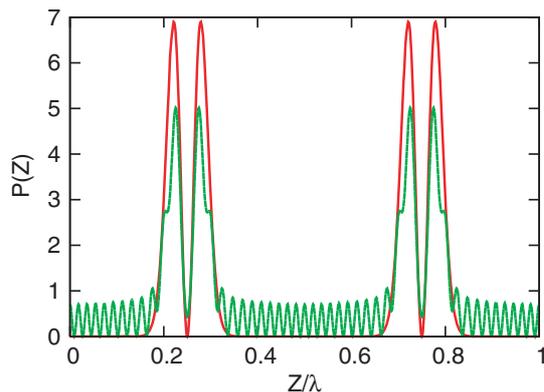
**Figure 3.** The non-adiabatic coupling terms  $\partial\Phi(Z, R, 0)/\partial R$  and  $\partial\Phi(Z, R, 0)/\partial Z$  for  $\text{Na}_2$  in the vicinity of one of the periodic array of CIs shown in figure 2. These terms become singular at the CI point. The laser parameters used are the same as in figure 2.

Having discussed conceptual properties of light-induced CIs in some detail, let us discuss now the impact these intersections might have on the ability of trapping cold diatomic molecules by light. A relevant quantity to be looked at is the probability  $P(Z)$  of finding the diatomic molecule at a given position  $Z$ , integrated over the rovibrational coordinates  $(R, \theta, \varphi)$  and over the electronic degrees of freedom. Formulated mathematically, if  $\vec{\Psi}(Z, R, \theta, \varphi) = [\Psi_0(Z, R, \theta, \varphi), \Psi_1(Z, R, \theta, \varphi)]$  is a Bloch eigenstate of the translationally periodic Hamiltonian (2), then  $P(Z)$  is obtained from

$$P(Z) = \int_0^\infty dR \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi \{ |\Psi_0(Z, R, \theta, \varphi)|^2 + |\Psi_1(Z, R, \theta, \varphi)|^2 \}. \quad (7)$$

Note that since the Hamiltonian is a  $2 \times 2$  matrix operator, its eigenvector has two components  $\Psi_0$  and  $\Psi_1$ . The better the molecules are considered to be trapped the more  $P(Z)$  exhibits pronounced spatial localization, which is of course periodic due to the spatial periodicity of the standing laser wave. Obviously, a molecule which is not trapped will have a probability  $P(Z)$  completely smeared out over  $Z$ . In order to search for non-adiabatic effects in  $P(Z)$  which may be attributed to CIs, we have performed two distinct kinds of calculations. In the first one, we have evaluated  $\vec{\Psi}(Z, R, \theta, \varphi)$  and  $P(Z)$  fully by solving numerically the Schrödinger equation for  $\hat{H}$  given by (2). In the second calculation, we have approximated  $\vec{\Psi}(Z, R, \theta, \varphi)$  by making the adiabatic separation for the coordinate  $Z$  from the remaining degrees of freedom. More precisely, in this  $Z$ -adiabatic approach we have neglected the non-adiabatic couplings associated with the translational motion, but kept all the non-adiabatic couplings between the vibrational and electronic motions.

To demonstrate the impact of the laser-induced CIs on trapping efficiency, we assume that the molecules are prepared in such a particular eigenstate of the full Hamiltonian (2) which is reduced to the  $X^1\Sigma_g^+(v = 3, J = 0)$  zero translational



**Figure 4.** Laser trapping of  $\text{Na}_2$  molecules prepared initially in their  $X^1\Sigma_g^+(\nu = 3, J = 0)$  rovibronic state. Shown are the probability distributions  $P(Z)$  to find a molecule at position  $Z$ . The laser intensity is  $I = 0.25 \text{ W cm}^{-2}$ . For more details, see text. The red curve displays the probability distribution computed within the  $Z$ -adiabatic approximation, in which the translational coordinate  $Z$  is adiabatically separated from the other nuclear degrees of freedom. The green curve displays the numerically exact result. The trapping efficiency is significantly reduced here due to the presence of non-adiabatic couplings which are singular at the CI points.

kinetic energy field free molecular state as the laser is turned off. Correspondingly, the laser frequency  $\omega_L$  is detuned by 2 MHz from the  $X^1\Sigma_g^+(\nu = 3, J = 0) \rightarrow A^1\Sigma_g^+(\nu = 4, J = 1)$  transition. The used field intensity is  $I = 0.25 \text{ W cm}^{-2}$ , even somewhat weaker than the laser intensities used routinely for trapping cold atoms, but still comparable with the laser intensity used, e.g. in the NIST cold atom experiment [19]. Importantly, the mentioned light intensity is large enough to support trapping of about 10 molecular states inside the lattice.

The results of our calculations of  $P(Z)$  for the first excited translational Bloch state are collected in figure 4 which shows that due to non-adiabatic effects the efficiency of molecular trapping can be significantly reduced. The impact of the laser-induced CIs can be expected to be substantially more dramatic if the molecules initially have sizeable translational energy. With growing initial translational energy, the numerical effort to solve the Schrödinger equation for  $\hat{H}$  in (2) also increases dramatically and new computational methods will have to be developed to attack the problem.

Before concluding we wish to comment on the difference between the trapping of atoms and trapping of molecules by standing laser waves. Trapping of atoms by standing laser waves requires an off resonance condition, i.e., the photon energy  $\hbar\omega_L$  must be slightly detuned from the atomic excitation energy. In other words, it is crucial to have the photon energy  $\hbar\omega_L$  either smaller (red detuned) or larger (blue detuned) than the excitation energy from the ground electronic state of an atom to its first symmetry allowed electronic excited state. In the case of a diatomic molecule the electronic excitation energies  $E_{0,1}(R)$  vary with the internuclear distance  $R$ . Therefore, it might happen that although the laser frequency  $\omega_L$  is detuned from the resonance condition at the equilibrium internuclear distance, it is in resonance for another internuclear distance (see figure 1 for a concrete example). In our paper,

we show for the first time that at such values of  $R$  (and for the accompanying specific values of the centre-of-mass coordinate  $Z$  and/or the rotational angle  $\theta$ ) the molecular electronic states dressed by laser light exhibit the topology of a light-induced conical intersection. This is a newly discovered phenomenon which may occur only for molecules and not for atoms. For nuclear geometries in the vicinity of such a conical intersection, the nuclear dynamics is intricately coupled with the electronic dynamics, due to the fact that the non-adiabatic coupling terms become singular (infinitely large) at the conical intersection points. The coupling becomes stronger and more significantly spoils the trapping of the molecules by light the more the populated molecular vibrational wavefunction ‘penetrates’ into the conical intersection region. The just mentioned light-induced non-separability between electronic and nuclear motions does not exist in the case of atoms. Its novel implications for reducing the efficiency of molecular trapping has been demonstrated numerically in the present work (see figure 4). In passing we note that, for such diatomic molecular systems where the relevant excited electronic state  $E_1(R)$  is purely repulsive, one encounters molecular dissociation stimulated by conical intersections. Another possible manifestation of the light-induced conical intersection effects may be perhaps found, e.g. in the context of molecular bond softening and hardening for intense laser fields [20, 21].

Summarizing the content of the present work, we have demonstrated theoretically that a laser interacting with a diatomic molecule generates an optical lattice which contains a *periodic array of light-induced CIs*. This is a novel and physically interesting phenomenon. At these intersections the non-adiabatic couplings become singular and the translational motion of the molecules becomes non-separable from their internal motions (electronic, vibrational, rotational). This should have many implications concerning the dynamics of cold molecules in standing laser waves. In particular, electronic, vibrational and rotational energy can be converted into translational energy and vice versa. As an illustrative example we studied ultracold  $\text{Na}_2$  molecules trapped by the standing laser wave. The calculations show that the strong non-adiabatic effects can make trapping difficult. In order to be able to control cold molecules in laser light in the future, it will be necessary to investigate the laser-induced CIs and the ensuing dynamics in great detail. We hope that our findings will motivate such investigations.

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