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On the feasibility of an ultrafast purely electronic reorganization in lithium hydride

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Abstract

Excitation of a coherent electronic wave packet, a linear combination of several electronic stationary states, is discussed with a computational example, the A and B low lying excited states of LiH. Such linear combination results in the electron executing a rotation-like motion in the xz plane with a period of 4 fs. The excitation needs to be shorter than this purely electronic reorganization time and yet the mean energy of the photon should be relatively low so that the A and B states are coherently accessed. These two requirements limit the wave form of the few cycle pump pulse.
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1. Introduction

LiH is viewed as 'the workbench of theoretical chemistry' [1]. Already quite early, Mulliken [2] drew attention to the electronic state switching as a function of nuclear coordinates and his Fig. 1 is since reproduced in many books. The more recent work including spectroscopic studies has been reviewed by Stwalley and Zemke [1]. Our earlier work [3,4] showed that upon sudden ionization of a neutral molecule one does access a coherent superposition of the electronic states of the cation. Such an electronic coherent state is non-stationary resulting in the hole migrating along the molecular backbone of the cation. The issue of principle in this paper is whether it is possible to access an electronic coherent state of the neutral molecule, starting from the ground state. Our aim is to explore this possibility at an elementary level and we use LiH as a concrete example.

That the motion of the nuclei results in extensive reorganization of the electronic charge distribution of LiH has been pointed out early on by Mulliken [2]. Here, however, we discuss a post-Born–Oppenheimer regime where the motion of the electrons occurs because we pump a non-stationary electronic state, and therefore, the electronic reorganization does not require the nuclei to move. As such, what we discuss is quite different from the failure of the Born–Oppenheimer approximation at a conical intersection [5–9] or at an avoided curve crossing [10], a failure induced by the motion of the nuclei [11]. The additional reason [3] for looking at such ultrafast process is that by controlling the coherent motion on several electronic states one may be able to control the motion of the nuclei and thereby manipulate the chemical outcome.
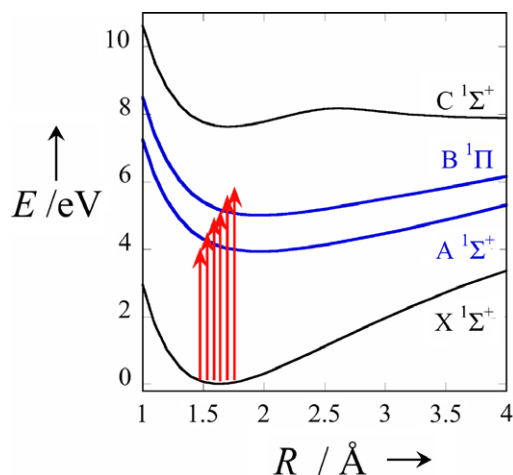

Fig. 1. LiH electronic energy vs. interatomic separation for the lower electronic states. Computed as discussed in Section 2. In the Franck Condon region the A and B states are separated by ≈1 eV. The red arrows symbolize the coherent excitation of a superposition of the A and B states using a coherent superposition of photons of different frequencies. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

Interference between exit channels is at the heart of coherent control [12]. It is furthermore possible in the time or frequency domains to probe the interference of different electronic states [10,13,14] and to coherently excite superpositions of Rydberg states. What is new here is the emphasis on short time dynamics before the onset of nuclear motion.

We compute below a period of 4 fs for a purely electronic motion. Therefore, not too long after the onset of the purely electronic reorganization also the nuclei will start to move. One will then reach the most challenging regime where neither the electrons nor the nuclei are in a stationary state. Steering such dynamics towards interesting outcomes is likely to be the next major goal.

Our theoretical work is motivated by the spectacular progress in attosecond physics; see the recent papers [15–20] and references therein. Recent theoretical studies of ultrafast processes include the work on localization of electrons by the laser pulse [21], on LiCN [22], on ring currents [23,24] on the importance of correlation effects in charge migration [25,26] and on high field effects [22].

In this paper, we first discuss the requirements from the pump pulse and then we do so with special reference to LiH, a molecule with two active electrons and this allows us to achieve acceptable accuracy and yet easy interpretation. Two well separated low lying electronic states with different polarization and comparable large transition dipole makes this a theorist choice. That the two suitable excited states of LiH with allowed transitions from the ground state are relatively low in energy means that the pulse needs to be centered around 5 eV. In much more refined computations both the A and B states are a shade lower in energy but the energy gap between the A and B states remains 1 eV. The necessary technology is becoming

available [27] but the requirements do need to be delineated. We briefly discuss the computations of the electronic structure of LiH and then construct the coherent superposition of the A and B states that we propose to excite. Finally, we compute the time evolution of the coherent non-stationary state and explain both analytically and by snapshot images that the electron executes a rotational motion.

The results discussed in this paper do provide motivation for a possible experiment. Additional detailed work is however required. We need to know the effect of the pulse duration. We furthermore need to characterize not only the pump but also the probe pulse. In view of earlier developments [28–32] it is natural to suggest probing by XUV photoelectron spectroscopy as we have explored for the peptides [33]. We will need this probe pulse to be polarized with respect to the pump pulse. Lastly, we have the longer range goal of steering the electronic motion. For glycine, the ps time scale onset of nuclear motion following photoionization of different conformers is discussed in Ref. [34].

2. The pump pulse

To pump electronic states of neutral molecules by single photon excitation means that the carrier or central frequency of the pulse needs to be in the visible or UV range. We furthermore propose to pump a non-stationary electronic state. Such a state can always be represented as a coherent sum of stationary electronic states. These states are those that are identified by conventional high resolution spectroscopy and/or that are computed by the standard methodology of quantum chemistry. The simplest possible coherent state is a linear combination of just two stationary states and in the example that we study below these will be the A and B excited states of LiH (Fig. 1). Unless the laser field shown in Fig. 1 is very strong, the state of the molecule after the pulse will be a superposition of A and B states and the ground state of the molecule.

A constraint on the pulse that is obvious from Fig. 1 is that the range of photon frequencies that coherently make the pulse must span the energy difference, ΔE between the two electronic states so that both can be accessed. We now argue that it will be useful to have an even wider range of frequencies. The reason is that it is known and also it is shown below that the time evolution of such a state will be like $\cos(\Delta E t/\hbar)$. Taking practical units this time factor is $\cos((\Delta E(\text{eV})/27.2)(1000t(\text{fs})/24.2)) \approx \cos(\Delta E(\text{eV})t(\text{fs})\pi/2)$. So for an energy difference of 1 eV the period is 4 fs. The duration of the pulse is preferably not comparable but shorter than this period and so its bandwidth should be wider in energy than the energy difference ΔE.

The above considerations show that we require coherent broadband radiation extending into the UV. Recent experiments indicate that the spectrum of the few-cycle near-IR light (centered at 750 nm) can be coherently extended to
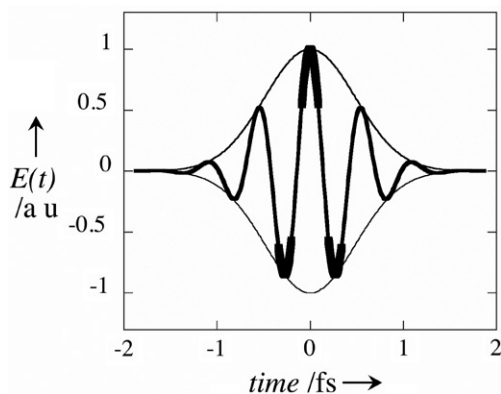
Fig. 2. A few cycle electric field, $E(t)$ in arbitrary units, at a frequency of $v = 30{,}000$ cm^{-1}, solid line confined to a Gaussian envelope, light line, vs. time in femtoseconds, shown as $\cos(2\pi v$ (in cm^{-1}) $3 \times 10^{-5}t$ (in fs))$\exp(-t^2/2\sigma^2)$. From the equation it is clear that a field at double the frequency can be confined by an envelope of half the width. The width used in the plot is $\sigma = 1$ fs. The width in frequency is about $(5300/\sigma$ (in fs)) cm^{-1}.

6 eV in the UV and offers the potential for being able to cover the entire spectral range of 1–10 eV [27]. Along with suitable elements for spectral amplitude and dispersion control, (which are available), this coherent UV/VIS/NIR supercontinuum will actually allow both the isolation of a Fourier limited excitation pulse with adjustable carrier frequency and bandwidth and the synthesis of (nearly) arbitrary optical waveforms. The former is what we need here for triggering dynamics by pumping an electronic wave packet and in general it is a very worthwhile challenge because the range from about 3 to 15 eV contains almost all of the spectroscopy of the valence electrons of molecules. The latter option is for the future because it will permit steering the subsequent motion.

For the proof of concept study, we propose pumping the A and B states of LiH as shown in Fig. 1. An ideal excitation pulse for this case is shown in Fig. 2. As this figure shows, we need pulses of the width in time of the order of 1 fs if they are to confine at least few cycles of 30,000 cm^{-1} (about 4.5 eV) photons.

It follows from Fig. 2 that to initiate a superposition of states that are further apart in energy requires a pulse that is narrow in time and so the few-pulse carrier electrical field that needs to be confined by the envelope has to oscillate at a higher frequency. A compromise is required when we want to reach a spectral range that is not too high in energy meaning a not high carrier frequency, yet we also want that the spacing in energy between the states that are coherently excited by the pulse be broad so that the excitation is impulsive as far as the nuclear motion is concerned.

3. Computational results for lower excited states of LiH

For LiH it is reasonable to freeze the 1s core electrons of Li and thereby treat the problem as that of two electrons.

Earlier workers have carried out extensive configuration interaction, CI, studies and pointed out that the stationary electronic states are a mixture of several electronic configurations, e.g., [35,36]. For the purpose of this paper, that is to provide a theoretical proof of concept for the experiment and to provide a simple physical interpretation we have carried out a limited CI using only singly excited Slater determinants. The electronic structure of the ground and lower excited states of LiH was computed at the CI/HF level using the Gaussian 03 suite of quantum chemistry programs [37]. At the CIS –HF/6-31G(d,p) level, we compute an equilibrium bond distance of 1.63 Å and a (unscaled by 0.89) vibrational frequency of 1379 cm^{-1}. Increasing the basis set size to 6-311G(d,p) gives an equilibrium value of 1.60 Å which is closer to the value reported [1] and a vibrational frequency of 1400 cm^{-1}. B3LYP/6-311++G(d,p) gives an equilibrium distance of 1.593 Å and frequency of 1409 cm^{-1}. For the excited states, CIS/HF-6-31G(d,p) places the A state at 4.089 eV above the ground state and the B state at 5.18 eV. (It must be borne in mind that because the nuclei will not move during an as excitation we compute all states at the equilibrium geometry of the ground state.) Going to CIS with a 6-311G(d,p) basis lowers the A and the B states by 0.1 eV, going to CIS(D) lowers the A and the B state by 0.3 eV but in both the cases they stay about 1 eV apart and, as discussed below, this is the number that is most relevant to us here.

Fig. 3 shows the isoamplitude contours of the MO's of the ground state that are accessed in the CIS computation of the $A^1\Sigma^+$ and the $B^1\Pi$ excited states. The main configurations that contribute to the two excited states are shown in Fig. 4. Either one of the two excited states has a bonding σ electron promoted to higher σ or π orbital.

For either the A or the B excited states of LiH there are primarily two configurations that are important. Eqs. (1)
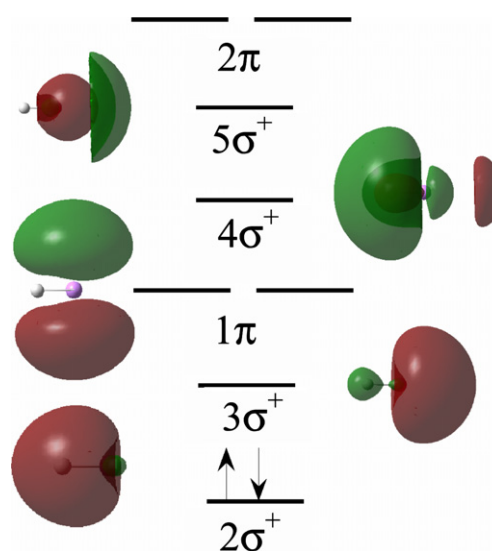

Fig. 3. Isoamplitude contours of the valence MO's of LiH computed at the HF/6-31G(d,p) level.
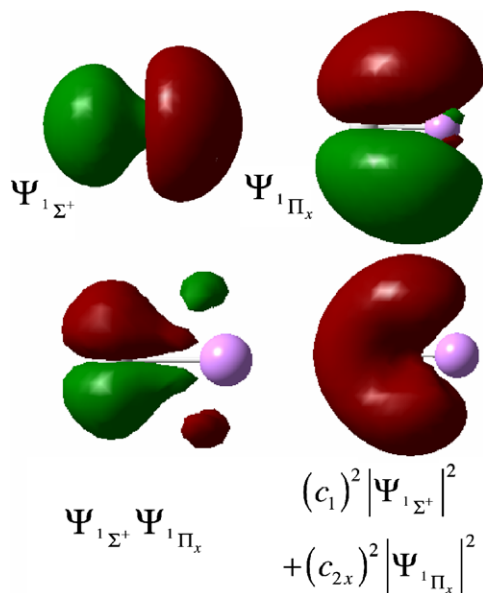
Fig. 4. Top: isocontour plots for the two wave functions $\Psi_{1_{\Sigma^+}}$ and $\Psi_{1_{\Pi_x}}$. Bottom: the product and sum of the squares of $\Psi_{1_{\Sigma^+}}$ and $\Psi_{1_{\Pi_x}}$ (see Eq. (5)). The molecular bond is along the z axis.

Fig. 5. Time evolution of the density of the electronic charge of LiH upon sudden excitation to a coherent superposition as shown at time $t = 0$.

and (2) list the orbital occupancy for the two main configurations that correspond to either one of these two excited states of interest.

$$\Psi_{1_{\Sigma^+}} = 0.69(2\sigma^+(1)3\sigma^+(2) + 2\sigma^+(2)3\sigma^+(1))$$
$$+ 0.15(2\sigma^+(1)5\sigma^+(2) + 2\sigma^+(2)5\sigma^+(1)), \tag{1}$$

$$\Psi_{1_{\Pi}} = 0.69(2\sigma^+(1)1\pi_x(2) + 2\sigma^+(2)1\pi_x(1))$$
$$+ 0.15(2\sigma^+(1)2\pi_x(2) + 2\sigma^+(2)2\pi_x(1))$$
$$+ 0.69(2\sigma^+(1)1\pi_y(2) + 2\sigma^+(2)1\pi_y(1))$$
$$+ 0.15(2\sigma^+(1)2\pi_y(2) + 2\sigma^+(2)2\pi_y(1)). \tag{2}$$

Fig. 4 shows the isoamplitude contour for the two wave functions $\Psi_{1_{\Sigma^+}}$ and $\Psi_{1_{\Pi_x}}$. The y component of the $^1\Pi$ state, $\Psi_{1_{\Pi_y}}$, is rotated around the molecular axis but is otherwise identical to (and degenerate with) $\Psi_{1_{\Pi_x}}$.

The higher molecular orbitals have p atomic character and so the optical transition from the ground state is strongly allowed. The transition dipole to the $^1\Sigma^+$ state is oriented along the z axis, while the transition dipole to the $^1\Pi$ state is oriented along the x, y axes. In the Franck Condon region the transition dipole satisfies $\mu_{1_{\Sigma^+}} \approx 0.3\mu_{1_{\Pi}}$. The $^1\Sigma^+$ and $^1\Pi$ states are about 1 eV apart. So it requires a pulse significantly shorter than about 4 fs, the period of a motion for $\Delta E = 1$ eV see Fig. 5, to prepare a coherent superposition of $^1\Sigma^+$ and the $^1\Pi$ states with weights in the ratio of about 1–3. This is just about possible. However, at the relatively low excitation energy of below 5 eV a slightly longer pulse envelope may be easier to achieve (cf. Fig. 2). But one can chose to prepare a superposition where the amplitude of the $^1\Sigma^+$ state is higher by using a somewhat longer pulse centered not quite midway between the states.
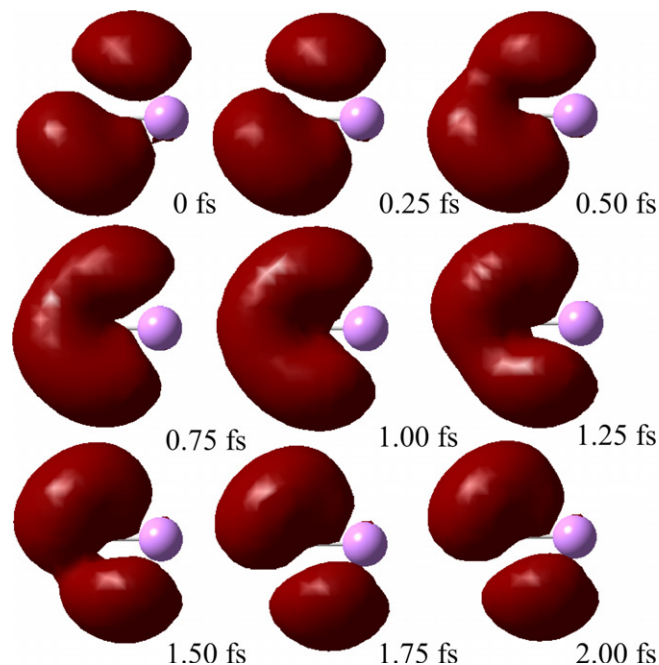
4. Ultrafast electronic excitation

To discuss the evolution of a coherent electronic state, we start at time zero with an excited state that is a superposition of the A and B states

$$\Psi(0) = c_1\Psi_{1_{\Sigma^+}} + c_{2y}\Psi_{1_{\Pi_y}} + c_{2x}\Psi_{1_{\Pi_x}}. \tag{3}$$

In a more refined treatment, see e.g., [33], one should recognize that the excitation is not really instantaneous but has a finite energy width. The very same treatment does however show that as long as the pulse width of the laser is shorter than the period of the electronic motion the approximation of a sudden excitation is semiquantitatively accurate. We further emphasize that the complete wave function of the molecule is a linear (coherent) combination of the ground and excited electronic state. About 5 eV energy difference between these two terms means that upon time evolution the interference term between them (cf. Eq. (4)) will beat with a period of about 0.5 fs and so will effectively average out at the time resolution of over 1 fs that we consider.

The coefficients in the linear combination [3] are determined by the relative transition dipole moments of the Σ and Π states and the orientation of the molecule with respect to the polarization of the laser.

In a beam the target ground state LiH molecules will be randomly oriented except possibly for some weak alignment induced during the supersonic expansion. However, by using a polarized laser it is possible to align the excited molecules [17].

Since for fixed nuclei the electronic states are eigenstates of the Hamiltonian, the early time evolution of the superposition as given by Eq. (3) is

$$\Psi(t) = \exp(-iHt/\hbar)\Big(c_1\Psi_{1_{\Sigma^+}} + c_{2y}\Psi_{1_{\Pi_y}} + c_{2x}\Psi_{1_{\Pi_x}}\Big)$$
$$= c_1\exp(-iE_{1_{\Sigma^+}}t/\hbar)\Psi_{1_{\Sigma^+}}$$
$$+ c_{2y}\exp\Big(-iE_{1_{\Pi_y}}t/\hbar\Big)\Psi_{1_{\Pi_y}}$$
$$+ c_{2x}\exp\Big(-iE_{1_{\Pi_x}}t/\hbar\Big)\Psi_{1_{\Pi_x}}, \qquad (4)$$

where the time-dependent phase factor is identical for the x and y terms.

To simplify the graphical presentation of the results, we take the molecules to be aligned and the laser to be circularly polarized such that only one of the two equivalent x or y components in Eq. (3) are excited. Fig. 5 shows the time evolution of the non-stationary coherent superposition created by the sudden excitation. With $\Delta E = E_{1_{\Sigma^+}} - E_{1_{\Pi_x}}$,

$$\Psi^*(t)\Psi(t) = (c_1)^2|\Psi_{1_{\Sigma^+}}|^2 + (c_{2x})^2|\Psi_{1_{\Pi_x}}|^2$$
$$+ 2c_1c_{2x}cos(\Delta Et/\hbar)\Psi_{1_{\Sigma^+}}\Psi_{1_{\Pi_x}}. \qquad (5)$$

The classical (first two terms) and interference (last term) contributions to Eq. (5) are shown in the bottom of Fig. 4. The figure uses color coding because the phase of $\Psi_{1_{\Pi_x}}$, and hence, of the interference term changes upon reflection in the zy plane where the molecular axis is along z.

Fig. 5 shows the time evolution of the density $\Psi^*(t)\Psi(t)$ for a series of values of time in the range of 0–2 fs showing that the (rotational) period of the electronic motion is 4 fs (rotational period meaning that the electron completes $v = 1/4$ rotations per fs as distinct from the angular velocity $\omega = 2\pi v$).

As seen in Fig. 5 and as expected from Fig. 4 and Eq. (5), the electron swings between the z and x axis. The phase of the oscillation of the charge is imposed by the polarization of the electric field of the laser.

We expect that probing the electron motion is possible with a second attosecond XUV pulse via ultrafast XUV photoelectron spectroscopy by measuring the angle-energy resolved spectrum of the photoelectron. A computed energy resolved spectrum was previously presented for the vibrational motion of the hole in peptide cations [3]. The reason why the present case may be easier to implement is that the ionization energy of electronically excited LiH is remarkably low and so it could be multiphoton ionized with few-cycle near-IR light or with a single photon from a second pulse of mean energy comparable to the pump pulse.

5. Concluding remarks

We discussed the theoretical possibility of pumping valence excited states of molecules with few-cycle laser pulses. A relatively unfavorable example was chosen as a test case, the two lowest optically accessible states, known as A and B, of LiH. The computations suggest that it is possible to induce a rotational motion of a valence electron in the LiH molecule by exciting a coherent superposition of these two electronically excited Σ and Π states. This rotational motion of the electron, Fig. 5, is somewhat slow with a period of 4 fs, but it is still fast as compared to the nuclear vibrational period of 24 fs. For the migration of a hole across a molecular backbone upon sudden ionization of peptides, we found earlier a period of 1.5 fs when the electron is removed from the HOMO [3,4,33]. Slower electron dynamics is computed also for the peptide when ionization removes a more deeply bound valence electron.

A rotational period of 4 fs means that the pump pulse envelope needs to be somewhat shorter than that. An envelope with a width of 1 fs and a mean frequency of $30,000\ cm^{-1}$ is not completely unreasonable as shown in Fig. 2 and the experimentally easier to realize wider width of 2 fs in the UV will be sufficient. Such pulses are available with demonstrated technology. Allowing for a Fourier limited excitation pulse for triggering the electronic motion is expected to be shortly available.

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