

Manipulating quantum entanglement of quasiparticles in many-electron systems by attosecond x-ray pulses

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Photoexcited electrons and holes in molecules or in semiconductors constitute a bipartite entangled system. We show that this entanglement can be coherently controlled by broadband x-ray pulses which create valence excitation wave packets through a stimulated Raman process. A novel measure of electron correlations in excited states is then provided by the time dependence of the concurrence. In a simulation study we demonstrate the control of entanglement of electrons and holes in CO that can be achieved by tuning a soft x-ray pulse to different core transitions: the carbon K edge (296 eV), the oxygen K edge (540 eV), and the $2\sigma \rightarrow 1\pi^*$ transition (191 eV).

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A bipartite quantum system in a pure state made of two distinguishable subsystems A and B is said to be entangled if the total wave function may not be factorized into a product of states in the two subspaces [1,2]. Entanglement is the basis for numerous applications to quantum computing, secure communication, and information processing. A key element in these applications is the ability to separately excite and probe the individual subsystems. This can be done either when they are physically separated (“Schrodinger cat” states) [3] or if they have different spectral properties (e.g., spins in molecules with different NMR chemical shifts) [4]. In this letter we show that electrons and holes in many-electron systems constitute an interesting bipartite system whose degree of entanglement may be coherently controlled on the attosecond time scale using newly developed x-ray sources [5–8]. Much attention has been devoted to probing the time evolving charge density with atomic spatial resolution by, e.g., x-ray diffraction or by watching the motions of holes created by XUV pulses [9,10]. However, x-ray pulses have the capacity to control phase coherence of many-electron wave functions that goes far beyond the charge density alone. For example, four-wave-mixing signals obtained with x-ray pulses can monitor the couplings between various parts of a molecule and contain some direct signatures of orbital delocalization [11]. Cross peaks in coherent two-dimensional signals reveal how two atoms (e.g., nitrogen and oxygen) are coupled. These are attributed to orbital relaxation, i.e., the difference of orbitals with core hole on the nitrogen, on the oxygen or on both.

In this paper we examine the valence excitation wave packets prepared by an x-ray pulse using concepts developed in the field of quantum information. A broad-band x-ray pulse, tuned on resonance with an atomic core transition, can create a wave packet of valence excited states $|g'\rangle$ with energies $\varepsilon_{g'}$ through a stimulated Raman process (Fig. 1). This wave packet is initially localized in the vicinity of the atom selected by the resonant x-ray frequency and subsequently evolves in time and spreads across the molecule. The doorway wave packet created by this Raman process is given by [12]

$$|\psi(t)\rangle = \sum_{g'} D_{g'} \exp(-i\varepsilon_{g'}t) |g'\rangle \quad (1)$$

with

$$D_{g'} = \sum_f V_{g'f} V_{fg} \int \frac{d\omega_1}{2\pi} \frac{E_1^*(\omega_1) E_1(\omega_1 - \omega_{g'g})}{\omega_1 - \omega_{g'g} - \omega_{fg} + i\Gamma_f}. \quad (2)$$

Here $|f\rangle$ are core excited states, Γ_f are dephasing rates, V is the dipole operator, and $E_1(\omega)$ is the complex envelope of the x-ray pulse tuned on resonance with selected core transitions and whose bandwidth covers several valence electronic states $|g'\rangle$. This wave packet can be viewed as an entangled state of electrons and holes. The actual state prepared by the Raman process is a coherent superposition with the ground state $|g\rangle + |\psi(t)\rangle$. However, only the excited state component $|\psi(t)\rangle$ is of interest to the current applications and in the following it will be normalized to unity $\langle\psi(t)|\psi(t)\rangle = \sum_{g'} |D_{g'}|^2 = 1$.

The short (\sim femtosecond) core state lifetime serves as a convenient internal clock that has been effectively used in narrow-band frequency-domain x-ray resonant scattering or Auger spectroscopy to extract information on photodissociation or vibrational dynamics of molecules [13–15]. Here we use a stimulated x-ray Raman technique to compete with the Auger process and prepare a valence wave packet for times that are not limited by the core lifetime window. This wave packet can be actively manipulated and probed in the time domain by other pulses.

Consider a molecule whose ground state $|g\rangle$ is described by a Hartree Fock wave function (a single Slater determinant) and whose single-particle levels (orbitals) are divided into two groups: occupied (system A) and unoccupied (system B). The elementary optical excitations are electron hole pairs. For clarity we assume that the many-body valence excited states are given by superpositions of single electron-hole pair states. This assumption, known as the single configuration-interaction (CI) level of electron structure theory, is not essential for the following arguments. However, it will simplify the notation and allow us to make our point more clearly. We shall comment on this further below. We can now write

$$|g'\rangle = \sum_{ij} A_{g',ij} c_i^\dagger d_j^\dagger |g\rangle. \quad (3)$$

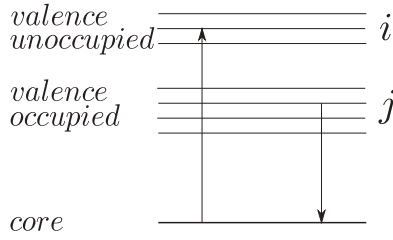


FIG. 1. Creation of a valence electron-hole pair excitation $|g'\rangle = c_i^+ d_j^+ |g\rangle$ by a stimulated x-ray Raman process. An attosecond x-ray pulse creates a coherent superposition of such states [Eq. (4)] which represents entangled electrons and holes. This wave packet is controlled by the choice of the resonant core orbital as well as the pulse envelope [Eq. (2)].

Here $c_i^+(d_j^+)$ are Fermi creation operations for electrons (holes). By combining Eqs. (1) and (3) we get

$$|\psi(t)\rangle = \sum_{i=1}^{d_A} \sum_{j=1}^{d_B} S_{ij}(t) c_i^+ d_j^+ |g\rangle \quad (4)$$

with

$$S_{ij}(t) = \sum_{g'} D_{g'} A_{g',ij} \exp(-i\varepsilon_{g'} t). \quad (5)$$

The indices i and j run over the d_A unoccupied and d_B occupied orbitals, respectively, and S_{ij} is a rectangular $d_A \times d_B$ matrix. The size of the relevant electron (d_A) and hole (d_B) spaces is generally different and will depend on orbital energies, selection rules, as well as the pulse bandwidth.

We next consider the reduced density matrix of the electron system (A) $\sigma_e = \text{Tr}_h |\psi\rangle\langle\psi| = S^+ S$. Its matrix elements are [16,17]

$$(\sigma_e)_{ik} = \sum_j S_{ij} S_{kj}^* = (S S^+)_{ik}. \quad (6)$$

Similarly, the reduced density matrix of the hole (B) system is $\sigma_h = \text{Tr}_e |\psi\rangle\langle\psi| = (S S^+)^T$, with the following matrix elements:

$$(\sigma_h)_{jl} = \sum_i S_{ij} S_{il}^* = (S^+ S)_{jl}. \quad (7)$$

We now use some well-known properties of bipartite systems. The Schmidt representation [2] is obtained by diagonalizing σ_e and σ_h and reads

$$|\psi(t)\rangle = \sum_{v=1}^d \sqrt{\lambda_v(t)} c_v^+(t) d_v^+(t) |g\rangle. \quad (8)$$

The $c_v^+(t)$ operators create Schmidt electron orbitals that diagonalize σ_e , whereas $d_v^+(t)$ create hole orbitals that diagonalize σ_h . They share the same eigenvalues $\sqrt{\lambda_v}$. The rank of this representation, i.e., the number of nonzero eigenvalues (d) is smaller or equal to the minimum of d_e and d_h . λ_v is the occupation probability of the v -th electron hole pair with the normalization $\sum_v \lambda_v = 1$. A convenient measure of the number of electron hole pairs participating in the wave packet is provided by $R = \text{Tr} \sigma_e^2 = \sum_v \lambda_v^2$. R^{-1} , known as the participation ratio, varies between 1 (no entanglement) to d (maximum entanglement). Concurrence $C = \sqrt{2(1-R)} = 2\sqrt{\sum_{v < v'} \lambda_v \lambda_{v'}}$ is

another measure of entanglement commonly used in quantum information applications [18,19]. The concurrence vanishes for a nonentangled state $d = 1$ and is finite for entangled states. For a given d , it has the maximum value $\sqrt{2(1-1/d)}$. If the electrons are uncorrelated, the excited states are given by single electron-hole pair excitations of the ground state involving Hartree Fock canonical orbitals, and the concurrence becomes time independent. The time dependence of the concurrence is therefore a useful measure of electron correlations in the valence excited states. It should be emphasized that we are not proposing a specific measurement since the concurrence is not a direct observable. Instead, we demonstrate how it may be effectively used in the simulation and analysis of measurements since it is characteristic to the dynamics of correlated optically excited states.

Femtosecond lasers in the visible can create electron-hole wave packets of Wannier excitons in semiconductors which are separated by ~ 10 meV. Electronic states in molecules are separated by a few eV. Due to their much narrower bandwidth, visible or UV pulses typically excite only one state at a time. This means that they select a single stationary electronic state $|g'\rangle$ in Eq. (1). S_{ij} [Eq. (5)] is then time independent and the entanglement is determined by the degree of correlation of the eigenstate and may not be manipulated. Thanks to their broad bandwidth, attosecond x-ray pulses can create valence electron-hole wave packets by the stimulated Raman technique.

The time-dependent concurrence can be manipulated by varying the pulse shape which may be optimized by coherent control techniques to meet desired goals [20]. Here we use a Gaussian pulse $E_1(\omega) = \exp[-(\omega - \omega_1)^2 / 2\sigma_1^2]$ with $\sigma_1 = 20$ eV and tune the carrier frequency ω_1 to different core transitions in CO. The core-hole broadening Γ_f was taken as 0.07 eV (0.10 eV) for carbon (oxygen) K edge [21]. For transition $2\sigma \rightarrow 1\pi^*$, Γ_f was estimated to be 0.06 eV.

We have simulated the time-dependent participation ratio and concurrence for three core transitions: the oxygen K edge ($\omega_1 = 540$ eV), the carbon K edge ($\omega_1 = 296$ eV), and a lower transition $2\sigma \rightarrow 1\pi^*$ ($\omega_1 = 191$ eV). Our calculations used a modified version of the package PSI3 [22] adapted to calculate the core excited states. The valence and core excited states were calculated with the minimal STO-3G basis at the single CI level. For the core excited states we obtained a set of relaxed orbitals using the static-exchange model [23] and used them in the single CI calculations. In Fig. 2, we show the time-dependent participation ratio for the first 10 fs. The main valence excited states that contribute to the signal are listed in Table I. In our model, CO has seven occupied and three unoccupied orbitals. Taking spin into account and recalling that the valence excited states are singlets, the minimum possible rank of the Schmidt decomposition (d) is 2 (this represents entangled spins). From Eq. (7), the maximum possible value of d is 6, corresponding to the maximum rank of σ_h (three orbitals with two possible spin values). From Table I, we see that two valence states dominate the oxygen and carbon K edge excitations. The $2\sigma \rightarrow 1\pi^*$ transition has three states. The different beat patterns reflect the degree of entanglement. The concurrence shown in Fig. 3 follows a similar pattern and varies between 1.00 [$\sqrt{2(1-1/d)}$ for $d = 2$] and 1.29 (when $d = 6$).

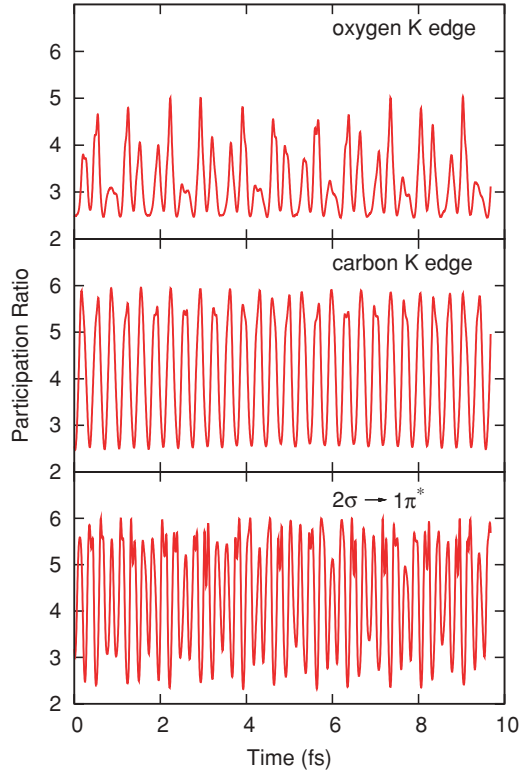


FIG. 2. (Color online) The time-dependent participation ratio R^{-1} of valence wave packets created by an x-ray pulse resonant with three core transitions of CO, as indicated. The transition frequencies from top to bottom are 540, 296, and 191 eV, respectively.

The Schmidt decomposition Eq. (8) forms the basis for the transition natural orbitals [16,24] which are commonly used to visualize optical excitations. Viewing the electron-hole wave packet as a bipartite system by considering the reduced electron and hole density matrices [Eqs. (6) and (7)] separately, rather than the transition density matrix offers a convenient means for characterizing many-body excited states. Signals obtained by various detection modes of the wave packet [Eq. (1)] using additional x-ray pulses or by detecting Auger electrons should be sensitive to the degree of entanglement.

The ability to manipulate entanglement is the key for quantum information processing applications [25,26]. Such control was demonstrated here on the attosecond time scale.

TABLE I. The six major valence excited state contributions to the valence wave packets prepared by the three core excitations used in the present simulations. The states $|g'\rangle$ are labeled in increasing order of energies (column 1).

$ g'\rangle$	$E_{g'}(eV)$	$ D_{g'} ^2$ (oxygen K edge)	$ D_{g'} ^2$ (carbon K edge)	$ D_{g'} ^2$ ($2\sigma \rightarrow 1\pi^*$)
4	10.69	0.03796	0.01182	0.00905
5	10.69	0.06269	0.01953	0.01495
8	19.56	0.06073	0.37849	0.44332
11	31.68	0.68598	0.58300	0.11670
14	36.50	0.15025	0.00051	0.38921
15	55.53	0.00240	0.00665	0.02677

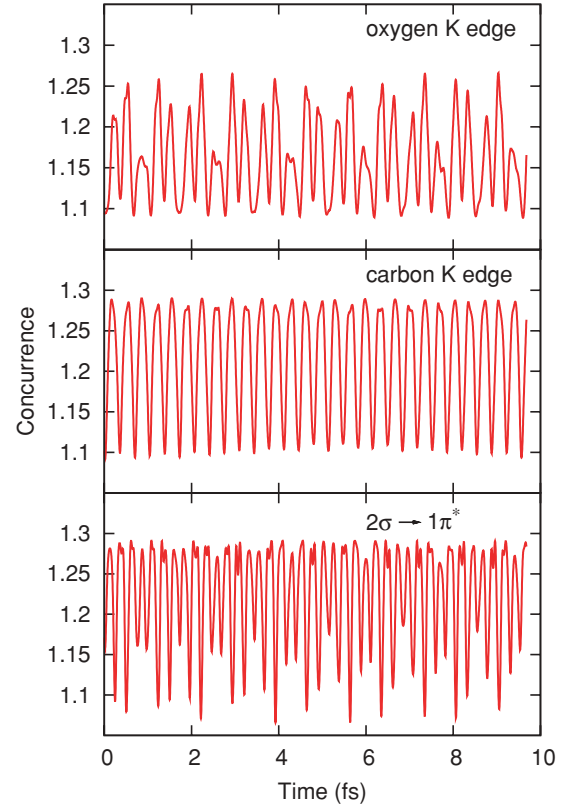


FIG. 3. (Color online) The time-dependent concurrence C corresponding to Fig. 2.

However, many challenges must be overcome before such applications could be realized. First, the usual schemes in NMR use strong π and $\pi/2$ pulses which transfer the system fully to the excited state. The x-ray excitations are perturbative and prepare the system in a superposition of the ground state and a small excited state component that carries the relevant information. The signals are thus weaker, and maintaining that coherence for longer time scales is not an easy task. Second, we have used an x-ray Raman process in order to create valence rather than core-hole excitations. The latter are short lived due to the femtosecond lifetime. Valence excitation lifetimes are picoseconds or longer. Eventually, the quantum information must be recorded in more robust ways than through valence electronic coherence so it can be stored and retrieved. Third, a scheme must be developed for reading the electrons and holes separately. This could be done by addressing the quasiparticles in energy space by optical fields resonant with either the electrons or the holes. We emphasize that the two subsystems considered here are the electron and hole quasiparticles and not the real electrons whose number can be arbitrary. The occupied and the unoccupied orbitals of the electron and hole subspaces constitute the relevant degrees of freedom and the entanglement is caused by their Coulomb interaction. Each active orbital accessible by the x-ray pulse acts as a qbit (since it can be either occupied or not).

Even though we only considered in Eq. (3) excited states with a single electron-hole pair, our arguments hold for an arbitrary number of pairs (two-exciton, etc.) as long as the ground state is noninteracting and the vacuum is given by a

single Slater determinant. This is because the electrons and holes form a bipartite system of quasiparticles irrespective of the number of electron hole pairs.

In summary, we have demonstrated how the manipulation and control of entanglement and many-body coherences may be used as a novel tool for the analysis of attosecond x-ray measurements and characterize the valence excitations. This type of analysis which goes beyond the time-dependent charge density may also be used for comparing different levels of theories of correlations in excited states of many electron systems. It may further be extended to

strongly correlated open systems with dissipation. For uncorrelated electrons the concurrence is static and its time dependence is induced by electron correlations. It therefore provides a sensitive and direct dynamical measure of electron correlations.

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