Electron dynamics in molecules is an emerging field of research driven by recent advances of attosecond time-resolved laser spectroscopies [1-4]. In particular, the high-harmonic generation (HHG) spectra induced by intense laser pulse has been a major subject [5-9] vitalized by a proposed possibility of self-probing molecules by their own electrons, which aims as far as to probe electronic wave functions (more precisely the Dyson orbitals) via the so-called molecular orbital (MO) tomography [10-13].

Theoretical studies of HHG spectra with quantum dynamical calculations of realistic systems have been rather limited to small atoms and molecules such as H, He, H$_2^+$, H$_2$, HeH$^+$, D$_2^+$, and LiH [14-19]. Treating more electrons in larger and more complex molecules seems too demanding at present unless invoking the time-dependent mean-field approximations of various levels [20-25] or the density functional theory (DFT) [27-29].

The conventional MO and DFT calculations are based on atomic orbitals (AOs) that are clamped at nuclear centers, with the time-dependence carried by the coefficients of MO or the configuration-interaction (CI). They essentially rely on the concept of one-electron orbitals in the mean-field, which are normally delocalized over the molecule according to its spatial symmetry. To describe the dynamics of delocalized wave functions by spatially fixed basis functions, those of large wave numbers or high angular momenta are needed.

To obtain an alternative perspective, we have been studying a model of localized electron wave packets (EWPs) with non-orthogonal valence-bond (VB) spin-coupling [30-33]. It was originally developed for a polarizable and reactive force-field model in condensed phase simulations to be combined with nuclear wave packets for light atoms [34-37]. The present work is a spin-off which demonstrates its utility for studying real-time quantum electron dynamics with practical and conceptual simplicities.

After an outline of the theory and computation, potential energy curves for electron motion in a LiH molecule are presented. Quantum electron dynamics on these potential curves induced by an intense laser pulse is computed and the resulting HHG spectra are examined. A non-conventional picture that depicts contributions from each of the Li 2s and H 1s electrons is presented.

The electronic wave function is assumed to be an antisymmetrized product of spatial and spin functions,

$$\Psi(1, \cdots, N) = A[\Phi(r_1, \cdots, r_N)\Theta(1, \cdots, N)],$$  \hspace{1cm} (1)

with the spatial part modeled by a product of one-electron functions,

$$\Phi(r_1, \cdots, r_N) = \phi_1(r_1) \cdots \phi_N(r_N).$$  \hspace{1cm} (2)

In contrast with the conventional VB methods that use the AOs clumped at nuclear centers, we employ spherical Gaussian WPs of variable position $q_i$ and width $\rho_i$,

$$\phi_i(r) = \left(2\pi\rho_i^2\right)^{-\frac{1}{2}} \exp[-|r - q_i|^2/4\rho_i^2].$$  \hspace{1cm} (3)

In our previous report [33], $q_i$ and $\rho_i$ were time-dependent, but in this work, the EWPs are used just to construct the potential energy curves along displacements of $q_i$ on which the full quantum dynamics are evolved.

The spin part $\Theta(1, \cdots, N)$ consists of the spin eigenfunctions. In this work, we employ a single configuration of the perfect-pairing form,

$$\Theta = \theta(1, 2)\theta(3, 4) \cdots \theta(N-1, N)$$  \hspace{1cm} (4)

with $\theta(i, j) = (\alpha(i)\beta(j) - \beta(i)\alpha(j))/\sqrt{2}$.

The ground state wave function and energy are computed by optimizing $q_i$ and $\rho_i$ to minimize the energy expectation, $E = \langle \Psi | \hat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$. The accuracy of the potential energy curve along the nuclear separation in the ground $X^1\Sigma^+$ state of LiH has been confirmed previously [32]. The EWP widths $\rho_i$ are then fixed at the optimal values, and energy variations by displacements of the EWP centers $q_i$ in the bond direction are computed to construct the potential energy curves. Although this is essentially a one-electron approximation under the field of other EWPs, it is distinct from those of MO and Kohn-Sham models. On these potentials, the full quantum dynamics of each electron are computed. The use of such EWP potentials is related to the coherent-state path-integral theory in which the Gaussian WPs are identified as the coordinate representation of the coherent-state basis and the action integral is determined by the energy expectation with respect to
FIG. 1: Potential energy curves for displacements of the wave packet centers in the singlet \(^1\Sigma^+\) state of LiH. The inset shows the wave packets represented by circles with the radius of wave packet width \(\rho_i\). It also removes the singularity of Coulomb potentials that can cause problems with numerical grids.

The electron dynamics are induced by a laser pulse with time-dependent electric field

\[ E(t) = E_0 \sin(\omega_0 t) \sin^2(\pi t/\tau), \quad 0 \leq t \leq \tau. \] (5)

The parameters were taken from Ref. [26]: the frequency \(\omega_0\) corresponding to the wavelength of 750 nm, the duration \(\tau\) of three optical cycles, \(\tau \approx 3(2\pi/\omega_0) \approx 7.51\) fs, and the field intensity \(E_0\) of \(5.5 \times 10^8\) V/cm with the laser intensity \(4.0 \times 10^{14}\) W/cm\(^2\). The length of the simulation box was taken to be 1200 bohr, with the transmission-free absorbing potential [40] of 120 bohr length at both ends. The wave functions were propagated with the Cayley’s hybrid scheme [41] with the spatial grid length of 0.2 bohr and the time-step of 0.01 au (\(\sim 0.24\) as). The norm of the wave function stayed unity with the deviation less than \(10^{-7}\) throughout the simulation. The HHG spectra were computed from the Fourier transform of dipole accelerations.

Figure 1 displays the potential energy curves for displacements of each EWP. Two of them are deeply bound to the Li nuclear center and correspond to the Li 1s core electrons. Their contributions to the HHG spectrum have been analyzed previously with the ordinary frozen-core approximation of the MO-CI approach [26]. Therefore, we focus on the more labile Li 2s and H 1s electrons with much shallower potential wells in Fig. 1. Indeed, it has been found earlier that quantization on the shallowest potential curve that corresponds to the Li 2s EWP gives semiquantitatively accurate excitation energies of the lowest few electronic excited states including the \(\Sigma\) and \(\Pi\) states in spin singlet and triplet [32].

The potentials for EWPs are modulated under the external laser field via the field-dipole interaction. The modulations at the maximum and minimum of the field Eq. (5) (see also the upper panel of Fig. 3) are displayed in Fig. 2. Those for the Li 2s EWP indicate that the electron dynamics will be directly driven by the laser field without energy barriers, whereas the H 1s electron will be basically bound near the proton but with possibilities of tunneling out in both directions. These pictures are confirmed in Fig. 3 that plots the evolutions of position expectation and its root-mean-squares (rms) deviation.

Figure 4 displays the HHG spectrum from the dynamics of Li 2s and H 1s electrons in Fig. 3. For comparison, data from the state-of-the-art time-dependent complete active space
(TD-CAS) CI calculation \[26\] was included. It is seen that the sum of the Li 2s and H 1s spectra well reproduces the TD-CASCI reference, especially the plateau up to \(\sim 50\) harmonic order (HO) and the cut-off. The difference between H 1s and Li 2s spectra should be a direct consequence of the potential shapes in Fig. 2. However, the picture would be non-trivial compared with what would be obtained from the conventional MO schemes in which the valence AOs of Li 2s and H 1s are intimately mixed.

We have presented a case for the practical and conceptual utilities of localized WP model with VB coupling for studying quantum electron dynamics. Although more case studies and some technical improvements for numerical efficiencies are still needed, we envisage that its applications will extend to other systems including electron conduction and optical responses in solids and other condensed matters.

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\[\text{FIG. 4: Fourier transforms of the dipole acceleration that give the high-harmonic generation spectra. The abscissa is the harmonic order \(\omega/\omega_0\). The TD-CASCI data is from Ref. \[26\].}\]

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