Supporting Information for:

Advanced capabilities of the PYXAID program: Integration schemes, decoherence effects, multi-excitonic states, and field-matter interaction.

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Section A: Derivation of the action the operators $\exp(iL_i^{(1)}dt)$ and $\exp(iL_{ii}^{(2)}dt)$

We present the detailed derivation of the action of the operators $\exp(iL_i^{(1)}dt)$ and $\exp(iL_{ij}^{(2)}dt)$ given by Eq. 9. Namely, we want to show that:

$$\exp(iL_i^{(1)}dt) = \exp\left(\alpha_i \cdot dt \cdot c_i \frac{\partial}{\partial c_i}\right) : c_i \to \exp(\alpha_i \cdot dt)c_i = \left[\cos\left(\frac{dt}{\hbar}\varepsilon_i\right) - i\sin\left(\frac{dt}{\hbar}\varepsilon_i\right)\right]c_i, \quad (A.1a)$$

$$\exp(iL_{ij}^{(2)}dt) = \exp\left(dt \cdot \beta_{ij}\left(c_{j}\frac{\partial}{\partial c_{i}} - c_{i}\frac{\partial}{\partial c_{j}}\right)\right) : \begin{pmatrix}c_{i}\\c_{j}\end{pmatrix} \rightarrow \begin{pmatrix}\cos(dt \cdot \beta_{ij}) & \sin(dt \cdot \beta_{ij})\\-\sin(dt \cdot \beta_{ij}) & \cos(dt \cdot \beta_{ij})\end{pmatrix}\begin{pmatrix}c_{i}\\c_{j}\end{pmatrix}.$$
(A.1b)

The derivation is based on the Taylor series representation of exponent followed by applying powers of the corresponding operators and subsequent manipulation of the resulting terms. The derivation of the action of the operators of the type $\exp(iL_i^{(1)}dt)$ is well-know in the field of non-Hamiltonian molecular dynamics. We present the derivation for this type of operators only for completeness:

$$\exp\left(\alpha_{i} \cdot dt \cdot c_{i} \frac{\partial}{\partial c_{i}}\right)c_{i} = \left[1 + \alpha_{i} \cdot dt \cdot c_{i} \frac{\partial}{\partial c_{i}} + \frac{1}{2!}\left(\alpha_{i} \cdot dt \cdot c_{i} \frac{\partial}{\partial c_{i}}\right)^{2} + \dots\right]c_{i} = c_{i} + \alpha_{i} \cdot dt \cdot c_{i} + \frac{1}{2!}\left(\alpha_{i} \cdot dt\right)^{2} \cdot c_{i} + \dots = \left[1 + \alpha_{i} \cdot dt + \frac{1}{2!}\left(\alpha_{i} \cdot dt\right)^{2} + \dots\right]c_{i} = \exp(\alpha_{i} \cdot dt)c_{i}$$
(A.2)

The derivation of the action, Eq. A.1b, is similar, but is slightly more complex. Also, unlike Eq. A.2, in which only one variable is affected, we now consider the action on the pair of variables:

$$\exp\left(\phi\left(c_{j}\frac{\partial}{\partial c_{i}}-c_{i}\frac{\partial}{\partial c_{j}}\right)\right)\binom{c_{i}}{c_{j}}=\binom{c_{i}}{c_{j}}+\phi\left(c_{j}\frac{\partial}{\partial c_{i}}-c_{i}\frac{\partial}{\partial c_{j}}\right)\binom{c_{i}}{c_{j}}+\frac{1}{2!}\left(\phi\left(c_{j}\frac{\partial}{\partial c_{i}}-c_{i}\frac{\partial}{\partial c_{j}}\right)\right)^{2}\binom{c_{i}}{c_{j}}+\ldots=$$

$$=\binom{c_{i}}{c_{j}}+\binom{\phi c_{j}}{-\phi c_{i}}+\frac{1}{2!}\binom{-\phi^{2} c_{i}}{-\phi^{2} c_{j}}+\frac{1}{3!}\binom{-\phi^{3} c_{j}}{\phi^{3} c_{i}}\ldots=\binom{\left(1-\frac{\phi^{2}}{2!}+\ldots\right)c_{i}+\left(\phi-\frac{\phi^{3}}{3!}\ldots\right)c_{j}}{-\left(\phi-\frac{\phi^{3}}{3!}\ldots\right)c_{i}+\left(1-\frac{\phi^{2}}{2!}+\ldots\right)c_{j}}\right)=$$

$$=\binom{\cos(\phi)}{-\sin(\phi)}\binom{c_{i}}{\cos(\phi)}\binom{c_{i}}{c_{j}}$$
(A.3)

where, for simplicity of notation, we use:

$$\phi = dt \cdot \beta_{ij} = -\frac{i \cdot dt}{\hbar} H_{ij} \,. \tag{A.4}$$

Section B: Derivation of the matrix elements for field-matter interaction Hamiltonian

We derive Eq. 13b of the main text, starting with Eq. 13a and using a number of assumptions and approximations. First, we transform Eq. 13a from the classical to the quantum version. Using the correspondence principle, $\vec{p} \rightarrow -i\hbar \vec{\nabla}$, and specifying the particle to be an electron (q = -e), one can write a semi-classical Hamiltonian describing the electronic excitation in response to interaction with an electromagnetic field (e.g. laser):

$$\hat{H}' = -i\frac{e\hbar}{m_e}\vec{A}(\vec{r},t)\vec{\nabla}.$$
(B.1)

From the practical point of view, one needs to compute matrix elements of the Hamiltonian:

$$H'_{ij} = -i\frac{e\hbar}{m_e} \langle \psi_i | \vec{A}(\vec{r}, t) \vec{\nabla} | \psi_j \rangle.$$
(B.2)

In many periodic DFT codes, including the QE package, the KS orbitals are typically represented by expansion in a plane-wave basis. In the momentum representation, the expansion takes the form:

$$\psi_{\vec{K},i} = \sum_{\vec{G}} c_{i,\vec{G}} e^{i(\vec{G}+\vec{K})\vec{r}},$$
(B.3)

Note that in this expansion, the units of the coefficients $c_{i,\bar{G}}$ are Bohr^{-3/2}, because they include the unit

cell dimension factor $\frac{1}{\sqrt{\Omega}}$ from an alternative formulation of the wavefunction expansion:

$$\Psi_{\vec{K},i} = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \widetilde{c}_{i,\vec{G}} e^{i\left(\vec{G}+\vec{K}\right)\vec{r}}, \tag{B.4}$$

where,

$$c_{i,\vec{G}} = \frac{1}{\sqrt{\Omega}} \widetilde{c}_{i,\vec{G}} \,. \tag{B.5}$$

For computing observables, it is convenient to normalize the wavefunctions first. Then, the coefficients $c_{i,\bar{G}}$ become unit-less (but change numerically), and the units of the observables coincide with the units of the operator.

In the current version of the PYXAID program we focus on a single k-point (Gamma-point, $\vec{K} = \begin{pmatrix} 0 & 0 & 0 \end{pmatrix}^T$). Then, the wavefunctions, Eq. B.3, can be simplified:

$$\psi_i = \sum_{\bar{G}} c_{i,\bar{G}} e^{i\bar{G}\bar{r}} \,. \tag{B.6}$$

Finally, to define a field-matter interaction, we need to specify the form of the vector field. Normally, it can be expressed as a combination of plane waves (e.g. Sun radiation) with possible modulation of their amplitudes (e.g. laser pulse). The vector potential in this case can be written as:

$$\vec{A}(\vec{r},t) = \sum_{\vec{k}} \left[\vec{A}_{\vec{k}}(t) \exp\left(i\left[\left(\vec{k},\vec{r}\right) - \omega_k t\right]\right) + \vec{A}_{\vec{k}}^*(t) \exp\left(-i\left[\left(\vec{k},\vec{r}\right) - \omega_k t\right]\right) \right],\tag{B.7}$$

where \vec{k} is the wavevector of each plane wave, related to its angular frequency ω_k by:

$$k \equiv \left| \vec{k} \right| = \frac{\omega_k}{c} \,. \tag{B.8}$$

The amplitude modulation is described by the $\vec{A}_{\vec{k}}(t)$ and $\vec{A}^*_{\vec{k}}(t)$ terms. Two common forms of the amplitude modulation are described in the main text.

With the assumptions mentioned above, the matrix elements of the perturbation Hamiltonian are given by:

$$\begin{aligned} H_{ij}^{*} &= -i\frac{e\hbar}{m_{e}} \left\langle \psi_{i} \left| A(\vec{r},t) \vec{\nabla} \right| \psi_{j} \right\rangle = \\ &= -i\frac{e\hbar}{m_{e}} \sum_{\vec{k},\vec{G},\vec{G}^{*}} c_{i,\vec{G}}^{*} c_{j,\vec{G}^{*}} \int e^{-i\vec{G}\vec{r}} \left\{ \vec{A}_{\vec{k}}(t) \exp\left(i\left[\left(\vec{k},\vec{r}\right) - \omega_{k}t\right]\right) + \vec{A}_{\vec{k}}^{*}(t) \exp\left(-i\left[\left(\vec{k},\vec{r}\right) - \omega_{k}t\right]\right) \right\} \vec{G}^{*} e^{i\vec{G}^{*}\vec{r}} d\vec{r} = \\ &= -i\frac{e\hbar}{m_{e}} \sum_{\vec{k},\vec{G},\vec{G}^{*}} \left\{ c_{i,\vec{G}}^{*} c_{j,\vec{G}}^{*} i\vec{G}^{*} \vec{A}_{\vec{k}}(t) \exp\left(-i\omega_{k}t\right) \int e^{i\vec{k}\vec{r}} e^{-i\vec{G}\vec{r}} e^{i\vec{G}^{*}\vec{r}} d\vec{r} + c_{i,\vec{G}}^{*} c_{j,\vec{G}}^{*} i\vec{G}^{*} \vec{A}_{\vec{k}}^{*}(t) \exp\left(i\omega_{k}t\right) \int e^{-i\vec{k}\vec{r}} e^{-i\vec{G}\vec{r}} e^{i\vec{G}^{*}\vec{r}} d\vec{r} \right\} = \\ &= -i\frac{e\hbar}{m_{e}} \sum_{\vec{k},\vec{G},\vec{G}^{*}} \left\{ c_{i,\vec{G}}^{*} c_{j,\vec{G}}^{*} i\vec{G}^{*} \vec{A}_{\vec{k}}(t) \exp\left(-i\omega_{k}t\right) \delta\left(\vec{k} - \vec{G} + \vec{G}^{*}\right) + c_{i,\vec{G}}^{*} c_{j,\vec{G}}^{*} i\vec{G}^{*} \vec{A}_{\vec{k}}^{*}(t) \exp\left(i\omega_{k}t\right) \delta\left(-\vec{k} - \vec{G} + \vec{G}^{*}\right) \right\} = \\ &= -\frac{e\hbar}{m_{e}} \sum_{\vec{k},\vec{G},\vec{G}^{*}} \left\{ c_{i,\vec{G}^{*}+\vec{k}}^{*} c_{j,\vec{G}}^{*} \vec{G}^{*} \vec{A}_{\vec{k}}(t) \exp\left(-i\omega_{k}t\right) + c_{i,\vec{G}^{*}-\vec{k}}^{*} c_{j,\vec{G}}^{*} \vec{G}^{*} \vec{A}_{\vec{k}}^{*}(t) \exp\left(i\omega_{k}t\right) \right\} \end{aligned}$$

Further simplifications can be made to obtain the result, Eq. B.9. First, using the relation

$$\vec{A}_{\vec{k}}^* = \vec{A}_{-\vec{k}}$$
 (B.10)

and the fact that the frequencies depend only on the magnitude of the wavevectors $\omega_{|\vec{k}|} = \omega_{|-\vec{k}|}$, Eq. B.9

can be simplified by reversing the summation order in the second part:

$$H'_{ij} = \frac{e\hbar}{m_e} \sum_{\vec{k},\vec{G}'} \left\{ c^*_{i,\vec{G}'+\vec{k}} c_{j,\vec{G}'} \vec{G}' \vec{A}_{\vec{k}}(t) \exp(-i\omega_k t) + c^*_{i,\vec{G}'-\vec{k}} c_{j,\vec{G}'} \vec{G}' \vec{A}^*_{\vec{k}}(t) \exp(i\omega_k t) \right\} = \\ = \frac{e\hbar}{m_e} \sum_{\vec{k},\vec{G}'} \left\{ c^*_{i,\vec{G}'+\vec{k}} c_{j,\vec{G}'} \vec{G}' \vec{A}_{\vec{k}}(t) [\exp(-i\omega_k t) + \exp(i\omega_k t)] \right\} = \frac{2e\hbar}{m_e c} \sum_{\vec{k},\vec{G}'} \left\{ c^*_{i,\vec{G}'+\vec{k}} c_{j,\vec{G}'} \vec{G}' \vec{A}_{\vec{k}}(t) \cos(\omega_k t) \right\} = .$$

$$= \frac{2e\hbar}{m_e} \sum_{\vec{k}} \vec{A}_{\vec{k}}(t) \vec{\mu}_{ij,\vec{k}} \cos(\omega_k t)$$
ere.
$$(B.11)$$

Here,

$$\vec{\mu}_{ij,\vec{k}} = \sum_{\vec{G}} c^*_{i,\vec{G}+\vec{k}} c_{j,\vec{G}} \vec{G} , \qquad (B.12)$$

is the transition dipole moment in the momentum representation (up to a coefficient). Note that, in general, $\vec{\mu}_{ij,\vec{k}}$ depends on the wavevector \vec{k} , thus giving different perturbation magnitudes for different excitation energies and crystal momenta. However, in most practical applications, the size of the molecular system *a* is notably smaller than the excitation wavelength $\lambda \sim \frac{1}{k}$. Therefore, the following (dipole) approximation is valid: $(\vec{k}, \vec{r}) << 1$ or, equivalently, $|\vec{k}| << |\vec{G}|$. This result immediately simplifies Eq. B.12 by removing the dependence on the excitation wavevector, leading to Eq. 14 of the main text. Eq. B.11 is the result present as Eq. 13 of the main text.

Section C: Derivation of the relations between fluence and the field modulation parameters

We review the basic relations between radiation fluence and vector potential. Then, we present specific relations for the two modulation protocols of the vector potential implemented in the current version of the PYXAID program – the simple pulse, and the saw-tooth protocol. Finally, we provide numerical estimates of the proportionality constants and pre-factors.

C.1 Basic relations

In our derivations of the general and specific relations below, we assume that the electromagnetic field is monochromatic, so that the vector potential can be written:

$$\vec{A}(\vec{r},t) = 2\vec{A}(t)\cos(\vec{k}\vec{r} - \omega t).$$
(C.1)

Further, we assume that the field propagates in the x direction of some external Cartesian coordinate system: $\vec{k} = k(1 \ 0 \ 0)^T$, and that it is linearly polarized, such that the vector potential has only one component, $\vec{A} = \begin{pmatrix} 0 \ A_y \ 0 \end{pmatrix}^T$. Under these assumptions, the Maxwell equations for the electromagnetic field, Eq. 12, lead to:

$$E_{y}(\vec{r},t) = -\frac{\partial A_{y}(\vec{r},t)}{\partial t} = -2[\dot{A}_{y}(t)\cos(kx - \omega t) + \omega A_{y}(t)\sin(kx - \omega t)], \qquad (C.2a)$$

$$B_z(\vec{r},t) = -2A_y k \sin(kx - \omega t).$$
(C.2b)

The x-component of the Poynting vector is then given by:

$$S_{x} = \frac{1}{\mu_{0}} E_{y}(\vec{r}, t) B_{z}(\vec{r}, t) = \frac{2A_{y}\dot{A}_{y}k}{\mu_{0}} \sin(2kx - 2\omega t) + \frac{4A_{y}^{2}\omega k}{\mu_{0}} \sin^{2}(kx - \omega t).$$
(C.3)

The units of *S* are W/m^2 , such that the quantity has the meaning of the instantaneous radiation power per unit area. The radiation intensity is given by averaging S_x over a time-period:

$$I = \langle S \rangle = \frac{2k}{\mu_0} \langle A_y \dot{A}_y \sin(2kx - 2\omega t) \rangle + \frac{4\omega k}{\mu_0} \langle A_y^2 \sin^2(kx - \omega t) \rangle.$$
(C.4)

Because we are using the dipole approximation $(\vec{k}, \vec{r}) \ll 1$, the above expression simplifies:

$$I = \langle S \rangle = -\frac{2k}{\mu_0} \langle A_y \dot{A}_y \sin(2\omega t) \rangle + \frac{4\omega k}{\mu_0} \langle A_y^2 \sin^2(\omega t) \rangle, \qquad (C.5)$$

The units of I are also W/m², but it has the meaning of the time-averaged power per unit area.

Further, one can compute the laser fluence (J/m² in SI units) by integrating *I* over the exposure time (e.g. laser pulse duration) τ :

$$F = \int_{0}^{\tau} \langle S \rangle dt , \qquad (C.6a)$$

or simply as:

$$F = I\tau \,. \tag{C.6b}$$

Note, that the sign of S may, in general, be negative. The negative sign implies radiation and energy loss. The positive sign indicated absorption and energy gain. Because we are only interested in absorption, we focus on the absolute value of the time-averages Poynting vector $|\langle S \rangle|$, rather than S itself:

$$F = \int_{0}^{\tau} \left| \langle S \rangle \right| dt = |I|\tau.$$
(C.6c)

C.2 Fluence for the step-function modulation protocol

The step-function modulation protocol is given by:

$$A_{y}(t) = \begin{cases} A_{y}, t \in \left[T_{m} - \frac{T}{2}, T_{m} + \frac{T}{2}\right], \\ 0, otherwise \end{cases}$$
(C.7)

In this case, the first term in Eq. C.5 vanishes and the second gives:

$$\left\langle A_{y}^{2}\sin^{2}(\omega t)\right\rangle = A_{y}^{2}\left\langle \sin^{2}(\omega t)\right\rangle = \frac{A_{y}^{2}}{2}.$$
 (C.8)

The last equality arises from the assumption that the pulse duration *T* contains an integer number of field oscillation periods:

$$T = nT_f \,, \tag{C.9a}$$

where

$$T_f = \frac{1}{\nu} = \frac{2\pi}{\omega} \,. \tag{C.9b}$$

In other words, the condition $T\omega = 2\pi n$ should be satisfied. In our implementation, the validity of such condition is verified before calculations. If the input parameters do not satisfy this condition, a warning is printed and the laser pulse duration, T, is adjusted downward with respect to n, that is to:

$$T_{adj} = T_f floor\left(\frac{T}{T_f}\right). \tag{C.10}$$

Using Eq. C.8 and C.6, we obtain:

$$F = I\tau = \frac{2A_y^2 \omega k}{\mu_0} T \Longrightarrow A_y = \left(\frac{F\mu_0}{2\omega kT}\right)^{1/2},$$
(C.11a)

or, equivalently:

$$F = I\tau = \frac{2\pi cA_y^2}{\lambda^2} T \cdot \left(10^7 \frac{A \cdot m}{V \cdot s}\right) \Longrightarrow A_y = \lambda \left(\frac{F}{2\pi cT} 10^{-7} \frac{V \cdot s}{A \cdot m}\right)^{1/2}.$$
 (C.11b)

For practical purposes, it is useful to present numerical estimates of the conversion prefactors. First, we estimate A_y if the fluence is 1 mJ/cm², the pulse duration time is 1 fs, and the wavelength is 1 nm:

$$A_{y} = 1 \cdot 10^{-9} m \left(\frac{10 \frac{J}{m^{2}}}{2\pi \cdot 3 \cdot 10^{8} \frac{m}{s} \cdot 10^{-15} s} 10^{-7} \frac{V \cdot s}{A \cdot m} \right)^{1/2} = 1 \cdot 10^{-9} m \left(23 \frac{V^{2} \cdot s^{2}}{m^{2}} \right)^{1/2} = 4.7958 \cdot 10^{-9} \frac{V \cdot s}{m} \cdot$$
(C.12)

In SI units the constant $\frac{e\hbar}{m_e}$ is:

$$\frac{e\hbar}{m_e} = \frac{1.6 \cdot 10^{-19} C \cdot 1 \cdot 10^{-34} J \cdot s}{9.11 \cdot 10^{-31} kg} = 0.1756 \cdot 10^{-22} \frac{C \cdot J \cdot s}{kg}.$$
(C.13)

Therefore,

$$\frac{e\hbar}{m_e}A_y = 4.7958 \cdot 10^{-9} \frac{V \cdot s}{m} \cdot 0.1756 \cdot 10^{-22} \frac{C \cdot J \cdot s}{kg} =$$

$$= 0.084 \cdot 10^{-30} \frac{V \cdot s \cdot C \cdot J \cdot s}{m \cdot kg} = 0.084 \cdot 10^{-30} J \cdot m =$$

$$= 0.084 \cdot 10^{-30} J \cdot m \cdot 6.24 \cdot 10^{18} eV / J \cdot 1.98 \cdot 10^{10} Bohr / m =$$

$$= 1.038 \cdot 10^{-2} eV \cdot Bohr$$
(C.14)

Summarizing, the following expression holds for the pulse modulation function:

$$\frac{e\hbar}{m_e}A_y = 1.038 \cdot 10^{-2} eV \cdot Bohr \cdot \lambda \left[nm \left(\frac{F[mJ/cm^2]}{T[fs]}\right)^{1/2}\right].$$
(C.15)

C.3 Fluence for the saw-tooth modulation protocol

The saw-tooth modulation protocol is defined by:

$$A_{y}(t) = \begin{cases} A_{y} \frac{t - (T_{m} - T/2)}{T/2}, t \in [T_{m} - \frac{T}{2}, T_{m}] \\ A_{y} \frac{(T_{m} + T/2) - t}{T/2}, t \in [T_{m}, T_{m} + \frac{T}{2}]. \\ 0, otherwise \end{cases}$$
(C.16)

In this case, the fluence is given by:

$$F = I\tau = A_y^2 \frac{2k}{\mu_0} |\sin(2\omega T_m) - \cos(2\omega T_m)| = A_y^2 \frac{4\pi}{\lambda\mu_0} |\sin(2\omega T_m) - \cos(2\omega T_m)| \Rightarrow$$

$$A_y = \left(\frac{F\mu_0}{2k|\sin(2\omega T_m) - \cos(2\omega T_m)|}\right)^{1/2} = \left(\frac{F\mu_0\lambda}{4\pi|\sin(2\omega T_m) - \cos(2\omega T_m)|}\right)^{1/2} .$$
(C.17)

The vector field amplitude is:

$$A_{y} = 0.316 \cdot 10^{-7} \left(\frac{F[mJ/cm^{2}]\lambda[nm]}{\left|\sin(2\omega T_{m}) - \cos(2\omega T_{m})\right|} \right)^{1/2} \frac{V \cdot s}{m}.$$
(C.18)

Similarly to the simple pulse modulation protocol, the estimate of the conversion prefactor in $\frac{e\hbar}{m_e}A_y$ is

given by:

$$\frac{e\hbar}{m_e}A_y = 0.316 \cdot 10^{-7} \frac{V \cdot s}{m} \cdot 0.1756 \cdot 10^{-22} \frac{C \cdot J \cdot s}{kg} =$$

$$= 0.555 \cdot 10^{-30} \frac{V \cdot s \cdot C \cdot J \cdot s}{m \cdot kg} = 0.555 \cdot 10^{-30} J \cdot m =$$

$$= 0.555 \cdot 10^{-30} J \cdot m \cdot 6.24 \cdot 10^{18} eV / J \cdot 1.98 \cdot 10^{10} Bohr / m =$$

$$= 6.857 \cdot 10^{-2} eV \cdot Bohr$$
(C.19)

Thus,

$$\frac{e\hbar}{m_e}A_y = 6.857 \cdot 10^{-2} \left(\frac{F[mJ/cm^2]\lambda[nm]}{|\sin(2\omega T_m) - \cos(2\omega T_m)|} \right)^{1/2} eV \cdot Bohr .$$
(C.20)