Comment on “How to observe coherent electron
dynamics directly”

The main results of Ref. [1] rely on the assumption of the
validity of Eq. (1) in Ref. [1]. In essence, that equation is
meant to establish a connection between the time-dependent
electron density of a nonstationary electronic system and the
observable x-ray scattering pattern associated with that
system. The authors of Ref. [1] claim that their Eq. (1)
rests exclusively on the assumption that the electronic
dynamics to be imaged are much slower than the duration
of the x-ray pulse employed to probe those dynamics. (This
is in addition to the assumption of nonresonant x-ray probe
conditions.) The purpose of this Comment is to point out that
Eq. (1) in Ref. [1] for an x-ray pulse shorter than the electron dynamics
to be imaged may be found in Ref. [2]. Therefore, we
consider the validity of the results of Ref. [1] questionable.
Particularly, it must be expected that the patterns in Fig. 5 of
Ref. [1] differ qualitatively from what would be found in
experiment.

Let us assume that the electronic wave packet of interest evolves freely, i.e.,

\[ |\Psi_i(x,t)\rangle = \sum_i \alpha_i e^{-iE_i t} |\Psi_i\rangle, \tag{1} \]

where |\Psi_i\rangle is an eigenstate of the electronic Hamiltonian, E_i is
the associated eigenenergy, and \( \alpha_i \) is a time-independent,
generally complex expansion coefficient. In order to make
things particularly transparent, let us assume that only two
electronic eigenstates—|\Psi_1\rangle and |\Psi_2\rangle—contribute to the
wave packet. Then, the expectation value of any observable
will oscillate periodically with the period \( T = 2\pi / |E_2 - E_1| \).
A probe pulse that can resolve these oscillations will
necessarily be shorter than \( T \); equally necessarily, such a
pulse has a spectral bandwidth that exceeds the energy splitting between |\Psi_1\rangle and |\Psi_2\rangle. This is obvious from
Fourier considerations, and it holds irrespective of whether \( T \)
is a femtosecond or much longer. It is fundamentally
impossible to make the spectral bandwidth of the incoming
x-ray beam small in comparison to the energy splitting
between |\Psi_1\rangle and |\Psi_2\rangle if one is using an x-ray pulse that is
short enough to resolve the dynamics associated with coherent superpositions of those electronic eigenstates. It
must therefore be expected that even if the x-ray scattering
detector has perfect energy resolution (a most optimistic
assumption), the scattering signal will involve an incoherent sum over all final states that are energetically accessible
within the spectral bandwidth of the incoming x-ray beam. A
careful analysis within the framework of quantum electrodynamics demonstrates that this is indeed the case [2],
leading, in general, to a failure of Eq. (1) in Ref. [1].

This failure is particularly easy to see if we assume, for
simplicity, that the only final states energetically accessible
are |\Psi_1\rangle and |\Psi_2\rangle themselves (a gross oversimplification in view of the nonuniform energy level structure in the
Coulomb problem). Then, for a probe pulse much shorter
than \( T \), the differential scattering probability per x-ray
pulse, at high photon energy, is

\[ \frac{dP}{d\Omega} = \zeta \int d^3x \int d^3x' \langle \Psi, t_d | \hat{n}(x) \times \{ |\Psi_1\rangle \langle \Psi_1 | + |\Psi_2\rangle \langle \Psi_2 | \} \hat{n}(x') |\Psi, t_d \rangle e^{iQ(x-x')}. \tag{2} \]

Here, \( \hat{n}(x) \) is the electron density operator, \( Q \) is the photon momentum transfer, \( t_d \) is the time at which the x-ray probe pulse scatters from the electronic wave packet (the pump-probe time delay), and the constant \( \zeta \) depends, among other things, on the spectrum of the incoming x-ray beam and on the
spectral response of the x-ray scattering detector. Equation (2) may be easily verified by using the results
of Ref. [2]. (One may arrive at the same conclusion by
applying the analyses of Refs. [3] and [4].) The key point
here is that the right-hand side of Eq. (2) cannot be written in the form

\[ \int d^3x \int d^3x' \langle \Psi, t_d | \hat{n}(x) |\Psi, t_d \rangle \langle \Psi, t_d | \hat{n}(x') |\Psi, t_d \rangle e^{iQ(x-x')}, \]

which, up to a prefactor, is Eq. (1) from Ref. [1] in the
notation employed here. In other words, the requirement of a short pulse—or slow electronic dynamics—does not
eNSure that the final state reached in the photon collision
process equals the electronic wave-packet state right before
the collision. Finally, we would like to mention that
analogous considerations have been shown to apply to
time-resolved electron scattering [5].

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