First Principles Determination of Electronic Excitations Induced by Charged Particles

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Abstract

In this paper, we derive and implement expressions within the linear response TD-DFT framework for rates of transition between the ground and excited states induced by an external point charge. Symmetry considerations are given for the coupling between electronic states of well defined parity in two extreme limits of the point charge’s position, and a general method to determine the conditions under which electric dipole selection rules hold for describing electronic excitations induced by point charges is presented. The point charge induced transition rates for particular electronic excitations from linear response TD-DFT were validated through comparison to excited state populations from real time TD-DFT simulations following an impulsive point charge perturbation, then evaluated on a three-dimensional grid to map their spatial dependence for a small polybenzoid. This method, when combined with information about excited state energy gradients, represents a first step toward an ab initio framework
for probing the structural response of materials under electron beam irradiation due to inelastic scattering.

1 Introduction

Most of the widely-applied ab initio approaches for the calculation/prediction of observables measured by optical spectroscopies fall under the umbrella of time dependent electronic structure theories (TD-EST). Electronic excitation energies and associated transition probabilities probed by linear absorption spectroscopy can be accessed in TD-EST formalisms either through direct simulation of the electronic dynamics in the time domain,1–8 or through application of response theory in the frequency domain.9–16 Time-dependent self consistent field (TD-SCF)17 methods, which include both time-dependent Hartree-Fock (TD-HF) and Kohn-Sham density functional theory (TD-DFT), are frequently employed in this context due to their favorable scaling with respect to system size. TD-DFT in particular exhibits one of the highest accuracy-to-expense ratios of all excited state electronic structure methods, allowing a first principles treatment of electronic excitations in relatively large systems.

In the time domain, or “real time” (RT) TD-EST simulation approach, excitation energies and transition probabilities are resolved by propagating a system initially prepared in its ground state forward in time following a “kick” from an impulsive electric field. Fourier transforming the expectation values of electric/magnetic multipole operators collected during the ensuing electronic dynamics gives access to the corresponding frequency-dependent polarizability tensors, the traces of which are proportional to rotationally-averaged cross sections for various photophysical processes.1,18–20 These same quantities can also be solved for directly to first order in the strength of a monochromatic time-dependent perturbation through linear response theory.16,21,22

Given the long-standing pervasiveness of TD-EST methods for modeling the optical excitation of materials, it is somewhat unexpected that their use to predict the electronic excitations induced by the passage of high-energy electrons hasn’t garnered a
similar level of interest. While the response of materials to the elastic scattering of electron beams from their nuclei has been increasingly modeled using *ab initio* molecular dynamics in the electronic ground state, these studies have ignored the electronic excitations promoted through concomitant inelastic electron scattering processes. Materials of sufficient size can be represented as continuous dielectric media characterized by their complex, frequency-dependent permittivities. The polarization induced by an electron beam in the material can then be determined through the solution of Maxwell’s equations. However, the discrete nature of the electronic spectrum of materials approaching the molecular scale necessitates an atomistic quantum mechanical treatment. Historically, the quantum mechanical description of materials irradiated by swift electrons has most commonly been formulated as a plane-wave scattering problem for the incoming electron. Modern first principles treatments of the scattering of charged particles by materials include multiple scattering Green’s function approaches with the material’s electronic structure approximated at varying levels of sophistication, as well as methods couched in the kinematic treatment of the scattering. However, Tsubonoya, Hu, and Watanabe have recently reported simulations of low-energy electron wave packet diffraction by graphene nanoflakes, in which the incident electron wave packet and material’s electronic degrees of freedom were co-propagated within a real time, real space TD-DFT framework.

A common application of computational methods for modeling the interactions between materials and swift charged particles is the simulation of electron energy loss spectra. In electron energy loss spectroscopy (EELS) experiments, the electronic structure of a material is probed by analyzing the distribution of energies lost by electrons in an electron beam by way of their interaction with the material. Most often, only beam electrons that are scattered by the material through very small semi-angles are collected in EELS experiments. When only these small momentum-transfer scattering events are measured, the selection rules for electronic transitions within the material are typically consistent with those for optical excitation in the long-wavelength limit that emerge from the electric dipole approximation. Computational methods geared
toward the simulation of EELS spectra generally treat the interactions between materials and beam electrons at this same level of approximation.

Of course, when a material interacts with a very distant charged particle, it experiences an electric field that is effectively homogenous over its entire volume (see Fig. 1). In the limit where the material and the charged particle approach infinite separation, the interaction between the external point charge and the material is completely captured by just the lowest order (dipole) term in its multipole expansion. Otherwise, the charged particles comprising the material can be close enough to the external particle to appreciate the point source nature of its associated electric field, and experience spatially inhomogeneous forces that are not solely described by the dipole term. So, outside of the regime in which the electron beam is focused far away from the material whose electronic structure it is interrogating (i.e. the “aloof” beam geometry), some of the beam electrons that interact with the material are inelastically scattered through larger angles. While the electric dipole approximation may suffice for the calculation of EELS spectra, a proper accounting of the larger angle inelastic scattering events that promote electronic transitions disallowed by electric dipole selection rules is mandatory to a complete description of the electronic response of materials perturbed by the impact of charged particles. EELS experiments which also measure beam electrons scattered (through non-dipole interactions) into larger angles, while less common, have also been reported.

Accurate \textit{ab initio} approaches for modeling the electronic response of materials to point-source electric fields are needed to provide insight into the mechanisms of damage sustained by materials during electron microscopy and spectroscopy experiments. In this study, we present a tractable first principles method based on TD-DFT for resolving the distribution of excited electronic states populated in a material following brief exposure to an external point charge. We apply both real time and linear response TD-DFT to model the response of some simple low-Z materials (an isolated carbide ion (C\textsuperscript{4−}), benzene (C\textsubscript{6}H\textsubscript{6}), and pyrene (C\textsubscript{16}H\textsubscript{10})) to a point charge perturbation. The full scalar potential of this point charge is included in the electronic Hamiltonian in lieu of
truncated multipolar expansions thereof. This is done in the same spirit as pioneering work from List et. al., where oscillator strengths for optical transitions were calculated using the full semiclassical matter-field interaction operator without resorting to multipolar expansion.\textsuperscript{50,51}

The remainder of this paper is structured as follows. We first describe an approximate method of accounting for beam electrons in the electronic Hamiltonian (section 2.1). We then provide an overview of the theoretical formalism on which the developed computational methods are built (section 2.2), and give the working equations for RT and LR TD-DFT (sections 2.3 and 2.4). Calculations of the carbide ion and benzene molecule are then presented across a range of separation distances between the ion/molecule and the perturbing point charge (sections 3.1 and 3.2). We go on to present a general method to determine the range of separation distances over which a point charge produces an uniformly polarized electric field from the vantage of a nearby material (section 3.3), thereby elucidating the conditions under which electronic transitions induced by charged particles adhere to electric dipole selection rules. As a final showcase of the utility of the methodology, we resolve the position-dependance

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{A graphical sketch of the range of validity of the electric dipole description of the interaction between an atom and an external point charge. Electric field lines are indicated in black, and negative(positive) atomic charge density in blue(red). Top panel illustrates the electric field from a distant point charge, which is essentially homogeneously dipolar over the volume of the atom. Bottom panel illustrates the inhomogenous electric field experienced by an atom when a point charge is placed near to its nucleus.}
\end{figure}
of point charge induced electronic excitation rates for a small polycyclic aromatic hydrocarbon (section 3.4), and conclude with perspective on future directions for the TD-EST description of electron beam induced excitations and structural modifications of materials (section 4).

2 Methodology

All calculations were performed in a locally modified version of NWChem.\textsuperscript{52,53} In addition to the LR and RT TD-DFT calculations of electronic excitations induced by the presence of point charges, NWChem was also used (unmodified) to optimize molecular geometries, calculate LR-TD-DFT excited state energy gradients,\textsuperscript{54} and produce real-space electron density data for ground and excited states.\textsuperscript{52} Atomic units (AU) have been used throughout this paper unless otherwise noted.

2.1 Impulse Approximation Description of Relativistic Electrons

The individual electrons comprising high energy (\(\sim 0.1\) MeV and above) electron beams are associated with vanishingly small de Broglie wavelengths, and can be safely regarded as point-like over all but the most minute of length scales. Furthermore, the average speed of electrons in materials is (except in the case of core electrons of heavier elements) a small fraction of the speed of light, so the scalar potential dominates in the interaction between external electromagnetic fields. As such, we omit terms in the matter-field interaction Hamiltonian involving the coupling between the beam electron’s associated vector potential and the momentum of the material’s electrons in the current study.

The Lorentz invariant expression for the scalar potential of a charged particle translating at constant velocity is given in the retarded timeframe by the Liénard-Wiechert potential.\textsuperscript{55} In the zero velocity limit, the Liénard-Wiechert scalar potential recov-
ers the classical electrostatic (Coulomb) potential. As a charged particle’s speed approaches that of light, however, the electric field it emanates decreases in intensity along its direction of propagation and increases (proportionately) in the transverse directions. In the ultra relativistic limit, the point charge’s associated electric field is nonzero only in the plane transverse to its velocity. In this case, only the portion of a charge distribution that lies in this plane is perturbed by the fast point charge at any given instant.

\[
\lim_{v \to c} \approx \begin{cases} 
\text{e}^- & t = t_0 \\
\text{e}^- & t \neq t_0 
\end{cases}
\]

**Figure 2.** Schematic showing the electrostatic impulse approximation to the electric potential of an ultrarelativistic electron utilized in the current study. A piecewise description of the scalar potential of a swift electron is adopted, in which the system experiences an impulsive electrostatic potential only at the time that the point charge would be passing through the plane containing the atomic center(s).

In this preliminary study, we will only consider the interactions of isolated atoms and planar molecules with swift electrons. For time-domain simulations of the response of these “flat” systems to the passage of an ultrarelativistic electron, the scalar potential can be qualitatively approximated by an electrostatic potential impulse activated at the instant that the beam electron enters the plane containing the atomic center(s) (Fig. 2). While this may be a somewhat crude approximation to the true potential experienced by a material subjected to a finite velocity beam, it is employed in the current study also for method validation purposes, since it is only under this treatment that the perturbation is restricted to transferring population from the ground to excited states (and not between excited states.) The final state from the RT-TD-DFT simulation

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of a material subjected to the impulsive point charge perturbation can therefore be compared directly to point charge induced transition rates evaluated within first-order time dependent perturbation theory (using Fermi’s golden rule and LR-TD-DFT.)

The operator, $\hat{V}$, for the electrostatic potential energy of a material exposed to a particle with charge $q$ located at position $r_{pc}$ is given by:

$$\hat{V}(q, r_{pc}) = \frac{q}{|\hat{r} - r_{pc}|},$$

where $\hat{r}$ is the position operator in the space of the material’s electronic coordinates. Conveniently, $\hat{V}(q, r_{pc})$ is already present in the electronic Hamiltonian in the form of the electron-nuclear attraction potential, so its matrix elements are immediately available to be used for our purposes here with no additional software development effort.

In an EELS experiment, each beam electron performs two essential tasks: it perturbs the material, and it reports on the final state of the material through its energy loss. In contrast, the state of the material is known at all times during the RT-TD-DFT simulations. This allows for a material-centric perspective of the inelastic scattering process to be adopted, where only the state of the material following its perturbation by an external point charge is considered. Disregard for the final state of the scattered electron motivates (in part) the choice to express the system’s electronic state in a basis of spatially-localized (Gaussian) functions, rather than the delocalized functions (e.g. plane waves) that would provide a more natural basis for the scattering states of the beam electron. The electronic states of molecular species and materials which lack long-range structural periodicity (e.g. nanoscaled, amorphous, polycrystalline or otherwise disordered materials) are also most quickly-convergent when expressed in a spatially localized basis, and even crystals idealized as infinitely-extended periodic lattices will have this periodicity lifted by the application of a point-source electric field.
2.2 The TD-DFT Formalism

As TD-DFT is now a well established method, we only provide a brief overview of the formalism and necessary working equations here and refer readers to references 57 and 13 for a complete derivation and review of the method. We present TD-DFT working equations assuming pure functionals here for brevity, since the extension to global hybrid functionals which include a fixed fraction of exact Hartree-Fock exchange is trivial and detailed elsewhere.\textsuperscript{53,58} In the Kohn-Sham (KS) density functional theory, the many-electron Schrödinger equation is recast as an effective one-electron problem for a fictitious system of non-interacting electrons (described by KS orbitals, \( \{ \phi_i \} \)) evolving under an external potential that is designed to produce the density \( (\rho(r)) \) of the fully-interacting system from that of the non-interacting one.\textsuperscript{59,60}

The equation of motion for the KS orbitals is the time-dependent Kohn-Sham equation:\textsuperscript{17,61}

\[
i \frac{\partial \phi_i(t)}{\partial t} = \hat{F}_\phi(t)
\]  

(2)

The KS operator, \( \hat{F} \), is:

\[
\hat{F} = \hat{h} + \int dr' \frac{\rho(r')}{|r - r'|} + \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)}
\]  

(3)

where:

\[
\hat{h} = -\frac{1}{2} \nabla^2 - \sum_{k=1}^{m} \frac{Z_k}{|r - R_k|}
\]  

(4)

and \( m \) is the number of nuclei in the system, \( R_k \) and \( Z_k \) are the coordinates and charge of the \( k^{th} \) nucleus, \( r \) are electronic coordinates, and \( E_{xc} \) is the exchange-correlation energy functional. In the spin-restricted treatment for closed-shell systems, the total density is given by:

\[
\rho(r) = 2 \sum_{i}^{\text{occ.}} |\phi_i(r)|^2
\]  

(5)
where the summation in Eq. (5) runs over all doubly-occupied KS orbitals. The KS orbitals can be expanded in a finite basis of contracted, atom-centered Gaussian functions, \{\chi_\mu\}.

\[
\phi_i = \sum_\mu C_{\mu i}(t) \chi_\mu
\]  

(6)

Henceforth, Greek characters (\(\mu, \nu, \lambda, \sigma\)) will index these basis functions, lowercase Roman characters (\(i, j/a, b\)) will index the (occupied/virtual) KS orbitals of the KS-DFT ground state, and capital Roman characters (\(IJ\)) will index the (all electron) energy eigenstates.

The one particle reduced density matrix (1RDM) \(P\) can be expressed in the contracted Gaussian function basis through the orbital expansion coefficients from Eq. (6):

\[
P_{\mu \nu}(t) = 2 \sum_{i}^{\text{occ.}} C^*_{\mu i}(t) C_{\nu i}(t)
\]  

(7)

The KS matrix elements are given in the contracted Gaussian function basis by Eq. (8).

\[
F_{\mu \nu}(t) = h_{\mu \nu} + \sum_{\lambda \sigma} P_{\lambda \sigma}(t)(\mu \nu | \lambda \sigma) + v_{xc, \mu \nu}
\]  

(8)

where:

\[
(\mu \nu | \lambda \sigma) = \int dr dr' \chi^*_\mu(r) \chi_\nu(r) \frac{1}{|r - r'|} \chi^*_\lambda(r') \chi_\sigma(r')
\]  

(9)

\[
v_{xc, \mu \nu} = \int dr \chi^*_\mu(r) \frac{\delta E_{xc}}{\delta \rho(r)} \chi_\nu(r).
\]  

(10)

The 1RDM and KS matrix can be re-expressed in an orthonormal basis, \{\chi'_\mu\}, by way of the symmetric Löwdin transformation:
\[ \mathbf{P}' = S^{1/2} \mathbf{PS}^{1/2} \]
\[ \mathbf{F}' = S^{-1/2} \mathbf{FS}^{-1/2} , \]

where \( S_{\mu\nu} = \int dr \chi_\mu^*(r) \chi_\nu(r) \). The TD-KS equation can be written in Liouville–Von Neumann form as an equation of motion for the 1RDM in the orthogonalized basis:

\[ i \frac{\partial \mathbf{P}'(t)}{\partial t} = [\mathbf{F}'(t), \mathbf{P}'(t)] \]

(11)

Expectation values of one-body operators and the electronic energy are calculated according to Eqs. (12) to (13) (where \( A_{\mu\nu} \) are matrix elements of an arbitrary one-electron operator, \( \hat{A} \), in the nonorthogonal, Gaussian function basis).

\[ \langle \hat{A} \rangle = \sum_{\mu\nu} P_{\nu\mu} A_{\mu\nu} \]  

(12)

\[ \langle E_{\text{ele}} \rangle = \langle \hat{h} \rangle + \frac{1}{2} \sum_{\mu\nu} \sum_{\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\nu|\lambda\sigma) + E_{\text{xc}} [\rho(r)] \]  

(13)

### 2.3 “Real Time” TD-DFT

The general solution to Equation (11) is given by:

\[ \mathbf{P}'(t) = \mathbf{U}(t_0, t) \mathbf{P}'(t_0) \mathbf{U}^\dagger(t_0, t) \]  

(14)

Evaluation of the matrix representation of the time evolution operator, \( \mathbf{U} \), requires time-ordered exponentiation (denoted in Eq. (15) by \( T\exp \)) of the KS matrix integrated over the interval \((t_0, t)\).

\[ \mathbf{U}(t_0, t) = T\exp \left( -i \int_{t_0}^{t} dt' \mathbf{F}'(t') \right) \]  

(15)

In this work, \( \mathbf{U} \) will be approximated by the (second order) Magnus expansion
The KS matrix carries time dependence even in the absence of any external perturbation through its dependence on the 1RDM $P'(t)$. However, the KS matrix may also be explicitly time-dependent through the addition of an external potential, $\hat{V}_{\text{ext}}(t)$, to the KS operator defined in Eq. (3). In Eq. (16), both modes of time dependence are indicated by the notation $F'(V'_{\text{ext}}(t), P'(t))$.

$$U(t, t + \Delta t) =$$

$$\text{exp} \left( -\frac{i \Delta t}{2} \left( F'(V'_{\text{ext}}(t), P'(t)) + F' \left( V'_{\text{ext}}(t + \Delta t), e^{-i \Delta t F'(V'_{\text{ext}}(t), P'(t))} P'(t) e^{i \Delta t F'(V'_{\text{ext}}(t), P'(t))} \right) \right) \right) + O(\Delta t^3) \quad (16)$$

The cost of a RT-TD-DFT time step is essentially equivalent to that of two iterations of the self consistent field method when Eq. (16) is employed to integrate the electronic Schrödinger equation. The population of the $I^{th}$ energy eigenstate, $\rho_I$, can be accessed indirectly through autocorrelation functions of the expectation value of observables (e.g. dipole moment) collected during the simulation according to the relation shown in Eq. (17) (See Appendix 1).

$$\mathcal{F} \left( \langle \mu(0) \mu(t) \rangle \right) (\omega) = \sum_{IJ} \rho_I \left| \langle \Psi_I | \hat{\mu} | \Psi_J \rangle \right|^2 \delta(\omega - \omega_{IJ}) \quad (17)$$

### 2.4 Linear Response TD-DFT

Starting from Eq. (11) and solving for the response of a system initially in its ground state to (first order in the strength of) a monochromatic perturbation yields a non-Hermitian eigenvalue problem known as the linear response TD-DFT (or “Casida’s”) equations, whose solutions are excitation energies, $\{\omega_I\}$, and one-particle transition densities $\{X^I, Y^I\}$ referenced to the SCF ground state.$^{13,21,58,67-69}$
\[ \begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = \omega \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} \] (18)

\[
A_{ia,jb} = \delta_{ij}\delta_{ab}(F_{aa} - F_{ii}) + (ia|jb) + (ia|f_{xc}|jb)
\]

\[
B_{ia,jb} = (ia|bj) + (ia|f_{xc}|bj),
\]

where:

\[
(ia|f_{xc}|jb) = \int dr dr' \phi^*_i(r)\phi_a(r)\frac{\delta^2 E_{xc}}{\delta \rho(r)\delta \rho(r')}\phi_b^*(r')\phi_j(r')
\] (19)

The ground to excited state transition moments for an arbitrary one-body operator can be evaluated in the LR-TD-SCF formalism according to Eq. (21).

\[
\langle \Psi_0 | \hat{V}(r_{pc}) | \Psi_I \rangle = \sum_{ia} V_{ia}(r_{pc})X_{ia}^I + V_{ai}(r_{pc})Y_{ia}^I
\] (21)

In order to map out the the dependence of the transition potentials between electronic energy eigenstates on the point charge position, \( r_{pc} \), one only needs to form \( \hat{V}(r_{pc}) \) for different \( r_{pc} \) and recompute its trace with the transition densities for each
transition of interest according to Eq. (21).

The point charge induced transition rates between the ground and excited states can be approximated by application of the (state-to-state) Fermi’s golden rule expression given in Eq. (22).

\[ w_{0I}(\mathbf{r}_{pc}) = 2\pi \left| \langle \Psi_0 | \hat{V}(\mathbf{r}_{pc}) | \Psi_I \rangle \right|^2 \]  

(22)

3 Results

In each TD-SCF calculation reported in this study, the atomic or molecular system was initialized in its optimized DFT ground state. For RT-TD-DFT simulations, the TD-KS equation was integrated according to Eq. (16) with a 0.05 AU time step for a total of 50,000 steps, yielding 2,500 AU of simulated electronic dynamics. With these simulation parameters, the electronic energy was conserved to within \(10^{-11}\) AU during the perturbation-free evolution. Impulsive point charge perturbations were applied as described in section 2.1 during only the first time step of each simulation. All spin-allowed excitations ranging from valence to core transitions were considered (i.e. no frozen core approximation was employed.) For molecular systems, geometries were optimized in the electronic ground state at the same level of theory employed in the LR/RT TD-DFT calculations.

In addition to performing time domain simulations of the impulsively-perturbed systems, the matrix elements of the point charge potential between the DFT ground state and LR-TD-DFT excited states were also evaluated to calculate Fermi’s golden rule electronic transition rates.

3.1 Dipole Approximation Validity at Large Distances

In three separate RT-TD-DFT/6-31g(d) simulations of the benzene molecule, an impulsive point charge perturbation was applied at a distance of 100 \(a_0\) from the molecular center of mass (COM) along each Cartesian axis, such that the associated electric field
is 0.0001 AU in magnitude at the COM. Frequency domain autocorrelation functions were computed from the dipole moment expectation values collected at each time step of the simulations. To gauge the similarity of perturbations experienced by a system from a distant point charge and an homogeneous electric field, analogous simulations were performed in which a 0.0001 AU homogenous electric field impulse polarized along each axis was applied to the system (in the same lab-frame as the previous simulations).

The rotational average of the (frequency domain) dipole autocorrelation function resulting from application of these two types of impulse perturbations are plotted in Fig. 3. While the same electronic excitations are promoted by the homogenous electric field and that of a distant point source, the excited state populations are not in quantitative agreement due to the inhomogeneity of the field strength from the point source over the volume of the molecule. Nevertheless, there are neither optically dark transitions that are promoted by the distant point charge nor optically bright transitions that are not enacted by the distant point charge perturbation, demonstrating that dipole selection rules for electron beam induced electronic excitation are upheld in the aloof beam geometry.

**Figure 3.** Rotationally-averaged, frequency domain dipole autocorrelation functions for benzene following application of a 0.0001 AU homogenous electric field impulse in $x$, $y$, and $z$ directions, as well as an impulsive point-source electric field from a particle of elementary charge placed 100 $a_0$ away from benzene’s center of mass (COM) along $x$, $y$, and $z$. 
3.2 Dipole Approximation Validity at Intermediate and Small Distances

A series of real time TD-DFT simulations were performed for an isolated carbide ion in which the impulsive point charge perturbation was applied at different distances from the carbide center of mass. The 6-31+g(d) basis set was utilized, since its extra set of diffuse functions for each (valence) angular momentum shell provides an adequate description of the carbide ion’s ground state electron structure, and also permits relatively large amplitude fluctuations in the electron density. The dipole autocorrelation functions reveal the changes in excited state population that result from applying the point charge perturbation at these different distances. The distribution of electronic energy eigenstates contributing to the superposition after the point source electric field perturbation is applied (Fig. 5) varies non-monotonically in the point charge’s placement. The strongly dipole allowed (see Tab. 1), parity inverting $2p \rightarrow 3s$ transition shows appreciable transition rates over large distances, while the rates of parity preserving transitions increase sharply with respect to the point charge’s proximity to the atomic center.

The Fermi’s golden rule transition rates from the ground to LR-TD-DFT excited states for particular transitions are also reported in Fig. 6 across a range of separation distances from the carbide COM. Since the perturbation is only applied during the first time step in the RT-TD-DFT simulations (and $\Delta t << \hbar / |V_0|$) rates/probabilities from the first order perturbation theory accurately capture the weights of each excited state contributing to the final state of the system from the time-domain simulations. The peak at $\sim 2$ eV (the $2p \rightarrow 3s$ transition), for instance, shows close to zero transition probability from LR-TDSCF at $\sim 1$ Å separation and essentially zero population in the RT-TD-DFT dipole autocorrelation function. More generally, the relative excited state populations encoded into the intensity of peaks in the dipole autocorrelation functions (Eq. (17)) are proportional to the transition probabilities from LR-TD-DFT, as indicated by the near unity correlation coefficient in the linear fit of the the dipole
autocorrelation function intensities and LR-TD-DFT transition rates shown in Fig. 4.

**Figure 4.** Plot of the dipole autocorrelation function intensities versus Fermi’s golden rule transition rates evaluated over a range of distance (0.5 Å to 5.0 Å) for the identified transitions, along with lines of best fit and corresponding coefficients of determination, \( R^2 \).

**Table 1.** Excitation energies and transition dipole strengths (mod. squared) for the dipole-allowed transitions of the carbide ion.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Energy (eV)</th>
<th>( | \mu_0 |^2 ) (AU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2p → 3s</td>
<td>2.3880</td>
<td>4.6093</td>
</tr>
<tr>
<td>2s → 3p</td>
<td>12.147</td>
<td>0.1373</td>
</tr>
<tr>
<td>2p → 4s</td>
<td>25.864</td>
<td>0.1661</td>
</tr>
<tr>
<td>2s → 4p</td>
<td>29.409</td>
<td>0.1443</td>
</tr>
<tr>
<td>2p → 3d</td>
<td>53.490</td>
<td>0.5178</td>
</tr>
<tr>
<td>1s → 3p</td>
<td>275.66</td>
<td>0.0060</td>
</tr>
<tr>
<td>1s → 4p</td>
<td>294.80</td>
<td>0.0103</td>
</tr>
</tbody>
</table>

To contextualize the findings of the *ab initio* results, consider the point charge potential matrix elements between states of well-defined parity in two extreme limits for the point charge’s position relative to the atomic center. The electric field that the atom experiences from a point charge at infinite separation distance approaches perfect spatial homogeneity, rendering it an effectively even (*gerade*) function of the center of mass coordinates of the atom. Conversely, a point charge residing at the atomic center of mass produces an odd (*ungerade*) electric field in this same coordinate system. Consequentially, both parity preserving and parity inverting transitions can
be induced by the point charge perturbation depending on its location relative to the inversion center.

The electrons occupying, for instance, the 2s orbital of carbide in its electronic ground state provide a tangible example of this behavior. When a repulsive point charge is placed in the interior of their spherically-symmetric probability density distribution, the expectation value of the force they experience will contain a nonzero component oriented outward (radially). In the limit where the negative point charge is placed directly at the atom’s center, the charge contributed by one proton is negated. In this limit, the eigenstates of the perturbed electronic Hamiltonian for carbide are (neglecting any nuclear spin-dependent terms) identical to the more loosely-bound states of the unperturbed boride ion. In terms of the energy eigenstates of our carbide ion, though, this corresponds to a transition to a state in which s orbitals of higher principle quantum number become populated. Parity preserving transitions such as these are forbidden by symmetry under the electric dipole approximation. The fact that they become strongly allowed under the full scalar potential of a perturbing charge as it is brought into close proximity to the atomic center (see Fig. 6 and Fig. 7) indicates that terms beyond the dipole in the multipolar expansion are required to recover the correct selection rules for electronic excitations under these conditions. The disagreement between transition dipole strength and EELS intensity for systems exhibiting inversion symmetry has been appreciated experimentally in the case of electron beam excitation of optically-dark localized surface plasmon resonances in metal nanoparticles and the hybridized modes of their dimers.

To summarize this section, we have shown that the proportionality between a point charge induced electronic excitation’s probability and the corresponding transition dipole strength is broken when the distance between the external point charge and the material’s bound electron density is small, showing zero dipole strength for transitions that are significantly allowed under the full electric potential of the point charge for certain positions (and vice versa.) This is the Fourier compliment to the well-known caveat that the electric dipole approximation is valid only in the small momentum
Figure 5. (left) Valence excitation region of the frequency-domain dipole autocorrelation function, $\mathcal{F} [\langle \mu(0) \mu(t) \rangle] (\omega)$ for separation distances between the carbide COM and point charge ranging from 0.5 to 5 Ångstroms. (right) Carbon k-edge region of the spectrum with differently scaled axes relative to valence region on left for clarity of presentation.

Figure 6. Fermi’s golden rule rates for representative transitions, $w_{0f}$, calculated according to Eq. (22) for the isolated carbide ion across a range of separation distances from the carbide’s center. For transitions involving $p$ and $d$ orbitals, the reported rates are the summed rates for all degenerate excitations.
However, since the position of a convergent electron beam can now routinely be controlled with sub-Angstrom resolution in modern aberration corrected scanning transmission electron microscopes, methods for determining the allowedness of electronic transitions for a given beam position may prove to be of considerable practical value.

### 3.3 Dipole Approximation Validity at Arbitrary Point Charge Proximity

A charged particle emanates an electric field with magnitude inversely proportional to the squared distance from the particle, so it is straight-forward to renormalize point charge induced transition rates, $w_{0f}$, at a given separation distance from the material’s center with respect to the electric field strength. In this way, the dependence of electronic transition rates on the degree of the electric field’s polarization inhomogeneity can be isolated. Point charge induced transition rates for the carbide ion (calculated at the same level of theory as in section 3.2) were renormalized with respect to the electric field intensity, and are plotted in Fig. 8 for representative transitions. Since the polarization of the electric field from a point source approaches homogeneity at large distances from the point source, the separation distance at which a renormal-
ized transition rate in Fig. 8 converges to its long distance asymptotic value indicates the critical distance where the electric field from the point charge becomes effectively homogenous over the volume of the transition density. For point charges positioned this distance or further from the material, the dipole description of the field polarization holds exactly. Optically bright transitions in Fig. 8 are distinguished from the dipole-forbidden transitions by their non-zero renormalized rates in the large separation distance limit. For the dipole-forbidden, but quadrupole-allowed $2s \rightarrow 3d$ transitions, the non-convergence of the renormalized rates at large distances is consistent with the dipole approximation’s inadequacy across all separation distances.

The range of separation distances over which the dipole approximation holds for a particular electronic excitation is ultimately determined by the spatial extent of the corresponding transition density. However, comparing the determined dipole approximation validity ranges and the radial electron probability density (Fig. 7) in the carbide ion suggests a general rule-of-thumb: terms beyond first order in the multipolar expansion can contribute non-negligibly to the transition probability whenever a perturbing point charge is placed into a region where a material’s electron density is substantially nonzero.

**Figure 8.** Fermi’s golden rule transition rates, $w_{0f}$, calculated with coupling matrix elements that have been multiplied by the square of the distance (from the atomic COM) at which they are calculated to renormalize them with respect to the corresponding electric field strength.
3.4 Point Charge Induced Electronic Excitation Maps

By evaluating the electronic excitation rates for different point charge locations in and around the volume of a material, the point charge positions which maximize a given transition rate can be identified. We demonstrate this here for the pyrene molecule described by the B3LYP/6-31g(d) model chemistry. The position-dependent transition rates, $w_{0I}$ (Eq. (22)), were evaluated on a regularly-spaced grid with 0.1 Å resolution, and are plotted as isosurfaces in Fig. 9. The position dependent breakdown of the dipole selection rules is again demonstrated for this molecular system, with transitions to excited states exhibiting zero transition dipole strength from the ground state becoming strongly allowed for certain point charge positions.

![Isosurfaces of point charge induced transition rates](image)

3.72 eV, $||\mu_0|| = 2.8$

3.79 eV, $||\mu_0|| = 3.5 \times 10^{-4}$

6.46 eV, $||\mu_0|| = 1. \times 10^{-10}$

(a) (b) (c)

Figure 9. Spatial dependence of the point charge induced transition rate ($w_{0I}$) from the ground to first (a), second (b), and third (c) excited singlet states of pyrene, presented as isosurfaces with isovalues indicated by color in AU.

One may suspect that for a given transition, regions in which electron density is depleted in the excited state (i.e. negative difference density relative to the ground state) would correspond to the regions where the probability of point charge induced transition would be large. After all, the effect of the negative point charge is to repel the like charged electron density. The difference densities (relaxed$^{74}$ excited state...
density minus the ground state density) of the three transitions for which the position-dependent point charge transition rates are plotted in Fig. 9 were calculated, and are shown as isosurfaces in Fig. 10. Electron density that is repelled by a point charge at a particular position must also be displaced into regions of positive difference density for strong interstate coupling, so the difference density shows only anecdotal correlation with the transition rate in Fig. 9. Knowledge of the difference density alone is therefore insufficient for predicting the position dependence of the point charge induced transition rates.

![Figure 10. Charge density difference isosurfaces (isovalue = ±0.001 e/Å³) for the three lowest energy transitions of pyrene (presented in the same order as Fig. 9.) Red(blue) indicates depleted(excess) density relative to the ground state.](image)

Finally, we have also evaluated the excited state energy gradients (at the ground state equilibrium geometry) in the three lowest energy excited states of pyrene. These excited state forces determine the intrinsic structural response of the material in the instants following the electronic excitation. With the combined knowledge of excited state forces and the spatial dependence of point charge induced electronic excitation probabilities, one can begin to determine where point charges should be placed (i.e. where an electron beam should be focused) in order to activate a particular local vibration through inelastic scattering. Since both the forces on nuclei and the barriers preventing rearrangement/isomerization can be qualitatively different in ground and excited electronic states), electronic excitation by beam electrons can provide a non-
destructive route to selectively manipulate the structure of materials. The formation of topological defects in graphene has been observed during transmission electron microscopy imaging with beam energies well below the knock-on threshold, suggesting a potential role for electronic excitations in facilitating the isomerization. While excited state vibrational evolution and nonadiabatic relaxation through conical intersections is a well-known mechanism for the photoisomerization of molecular systems (and photoinduced phase transitions in condensed matter), the potential for harnessing these processes to induce localized structural modifications in materials through selective electron beam exposure is yet to be widely appreciated. The ability to engineer local structural modifications of materials with convergent electron beams could represent a milestone on the pathway to atomically precise materials manipulation and manufacturing technologies.

![Figure 11](image-url)

**Figure 11.** Changes in forces on nuclei upon electronic excitation to the three lowest energy singlet excited states in pyrene (presented in the same order as Fig. 9.) Force vectors (given in AU, or $E_H/a_0$) are scaled identically for all three electronic transitions. Note that all forces lie in the plane of the molecule for these particular transitions.

4 Summary and Conclusions

In this paper, TD-DFT based methods for evaluating rates of point charge induced transitions between ground and excited electronic states of materials were presented.
The Fermi’s golden rule transitions rates calculated using linear-response TD-DFT were shown to be consistent with the final populations of excited electronic states from real time TD-DFT simulations following an impulsive point source electric field perturbation. A straight-forward method to gauge the quality of the electric dipole approximation for describing interactions between materials and external point charges at a given separation distance was also presented. It was shown that the dipole approximation fails to capture many allowed transitions in materials that exhibit inversion symmetry, and more generally that terms beyond the dipole in the expansion of the scalar potential are essential to a correct description of the selection rules except when the perturbing charge is located well outside of the material’s bound electron density (i.e. in the “aloof” beam geometry.) Finally, it was demonstrated how excited state energy gradient calculation can be leveraged to connect the electronic excitation induced by the point charge perturbation and the instantaneous vibrational response in the material. This represents a humble first step toward the theory-guided engineering of number-conserving (i.e. non-“sputtering”) structural transformations of materials mediated by inelastic electron scattering.

In followup studies, the Authors plan to utilize the methods detailed here to investigate the response of nanophase materials to electron beam perturbations. Extensions of the method to utilize the relativistically correct form for the scalar potential of a swift charged particle are also planned, as well as simulations of the coupled electronic and vibrational response of the material via a mixed quantum-classical dynamics scheme\(^{81,82}\) capable of reproducing electron beam induced structural modifications of materials.

### 4.1 Appendix A

The autocorrelation function of an operator, \(\hat{A}\), is an even function defined by:

\[
\langle \hat{A}(0)\hat{A}(t) \rangle = \lim_{t' \to \infty} \frac{1}{t'} \int_0^{t'} d\tau \hat{A}(\tau)\hat{A}(\tau + t) \quad (A.1)
\]
Expressing the product of operators $\hat{A}(\tau)\hat{A}(\tau+t)$ in the electronic energy eigenbasis, $\{\Psi_I\}$, and recognizing that energy eigenstate populations $\{\rho_I\}$ are constants of the motion for a closed system (rendering the microcanonical ensemble average and time average equivalent) gives:

$$\langle \hat{A}(0)\hat{A}(t) \rangle = \sum_I \rho_I \langle \Psi_I | \hat{A}(0)\hat{A}(t) | \Psi_I \rangle$$  \hspace{1cm} (A.2)

Resolving the identity and making use of the definition of the time evolution operator gives:

$$\langle \hat{A}(0)\hat{A}(t) \rangle = \sum_{IJ} \rho_I \langle \Psi_I | \hat{A}(0) | \Psi_J \rangle \langle \Psi_J | \hat{A}(t) | \Psi_I \rangle$$  \hspace{1cm} (A.3)

$$= \sum_{IJ} \rho_I \langle \Psi_I | \hat{A}(0) | \Psi_J \rangle \langle \Psi_J | \hat{U}(0,t)^\dagger \hat{A}(0)\hat{U}(0,t) | \Psi_I \rangle$$  \hspace{1cm} (A.4)

Since $\{\Psi_I\}$ are the solutions to the time independent Schrödinger equation, $\hat{H}\Psi_I = \Psi_I E_I$, the time evolution and (time-independent) Hamiltonian operators commute, the autocorrelation function expression simplifies to:

$$\langle \hat{A}(0)\hat{A}(t) \rangle = \sum_{IJ} \rho_I \langle \Psi_I | \hat{A} | \Psi_J \rangle \langle \Psi_J | \hat{A} | \Psi_I \rangle e^{-i(E_I-E_J)t}$$  \hspace{1cm} (A.5)

Defining $\omega_{IJ} = E_I - E_J$, letting $\hat{A} = \hat{\mu}$, and Fourier transforming yields Eq. (17) directly.

References


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