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The consequences of improperly describing oscillator strengths beyond the electric dipole approximation

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The interaction between a quantum mechanical system and plane wave light is usually modeled within the electric dipole approximation. This assumes that the intensity of the incident field is constant over the length of the system and transition probabilities are described in terms of the electric dipole transition moment. For short wavelength spectroscopies, such as X-ray absorption, the electric dipole approximation often breaks down. Higher order multipoles are then included to describe transition probabilities. The square of the magnetic dipole and electric quadrupole are often included, but this results in an origin-dependent expression for the oscillator strength. The oscillator strength can be made origin-independent if all terms through the same order in the wave vector are retained. We will show the consequences and potential pitfalls of using either of these two expressions. It is shown that the origin-dependent expression may violate the Thomas-Reiche-Kuhn sum rule and the origin-independent expression can result in negative transition probabilities. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4937410]

I. INTRODUCTION

The utility of a spectroscopic technique is greatly enhanced by theoretical models that provide a language through which to explain complex phenomena.[1] For many spectroscopies, the strength of the incident field is weak enough that it can be described as a classical perturbation on a quantum mechanical system. A Taylor expansion of the perturbed observable is often introduced and then truncated at some finite order to describe the interaction of the incident plane wave with the system. In this way, the system's properties can be described in terms of electric and magnetic multipoles.[2,3] Unfortunately, many properties become origin-dependent when described beyond the lowest order nonzero multipole. This is nonphysical and a potential pitfall when using multipole theory, as molecular properties should be origin-independent when described through infinite order. This non-physical origin dependence has prompted the development of schemes to minimize the origin dependence[4] and the derivation of fully origin-independent expressions[5–8] for describing observable molecular properties.

If the wavelength of the incident field is long compared to the size of the system, the Taylor expansion describing the system-wave interaction can be truncated at the first term. This is the well-known electric dipole approximation (EDA), so-called because the electric dipole is the relevant multipole for describing molecular properties. The EDA assumes that the magnitude of the incident field is constant over the length of the system and is commonly used to describe one-photon molecular absorption and emission processes. X-ray absorption spectroscopy (XAS) is an interesting case where the EDA is not always valid. The wavelength of the field can often be <1 nm and thus comparable to the size of a molecular system.

The most commonly used expression for describing XAS oscillator strengths truncates the Taylor expansion after the second term. This origin-dependent expression is often used in the atomic spectroscopy community.[9,10] There is no ambiguity when defining the origin in atomic spectroscopy and the origin-dependence of the expression is not often considered. However, origin-dependence of computational oscillator strengths is an unavoidable issue for modeling molecular XAS where there is no unambiguously correct way of defining the origin of a multi-atomic system. This issue becomes even more important as molecular XAS spectra nowadays can be computed routinely with low-scaling many-body methods, such as time-dependent density functional theory (TDDFT).[11–16]

Neese and co-workers have developed a scheme to minimize this origin dependence by using clever choices of the molecular origin.[4] In many ways, this is physically satisfying because the molecular origin is often chosen to be within the transition density of a given excitation and the Taylor expansion of the plane wave is expected to converge more quickly in this region. However, this only marginalizes the origin dependence problem and does not eliminate it completely. It has been recently shown that this origin dependence is due to an incomplete treatment of the oscillator strength through second-order in the wave vector and a rigorously origin-independent second-order expression has been implemented by Jacob and co-workers.[5] It is important to understand that these different oscillator strength expressions may lead to different interpretations and assignments of spectral features. There are also some important nuances, strengths, and deficiencies unique to these expressions that have yet to be explored in the literature. In fact, the use of either expression can lead to surprising consequences,

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highlighting the need for further developments in this field. In this work, we will compare the complete second-order oscillator strength expression with the more commonly used origin-dependent expression. Some of the most noteworthy consequences of using each expression that will be described in detail, including violation of the Thomas-Reiche-Kuhn (TRK) sum rule, varying spectral lineshapes and, most surprisingly, the possibility of having computed negative transition probabilities.

II. THEORY

The interaction of a molecular system with an electromagnetic field is often treated semiclassically.[17–19] The incident field is treated as a classical plane wave and the molecular system is described quantum mechanically. The incident electric field **E** is described by means of the scalar and vector potentials ϕ and **A**. We will assume the Coulomb gauge where $\nabla \cdot \mathbf{A} = 0$ and add the further constraint that the scalar potential be zero, $\phi(\mathbf{r}, t) = 0$. This particular choice of gauge is often referred to as the velocity gauge and we will make comparisons later to the so-called length gauge when discussing transition properties below.

A. The absorption of light

The Hamiltonian describing the interaction of a quantum system with a monochromatic electric field in the non-relativistic limit can be written as

$$\hat{H}(t) = \sum_i^N \frac{1}{2m_e} \left[\hat{\mathbf{p}}_i - \frac{e}{c} \mathbf{A}(\mathbf{r}_i, t) \right]^2 + V(\mathbf{r}_1, \ldots, \mathbf{r}_N), \quad (1)$$

where $\hat{\mathbf{p}}_i = -i\hbar\nabla$ and e and m_e are the charge and mass of the electron, respectively. The vector potential is defined as

$$\mathbf{A}(\mathbf{r}, t) = -A_0 \boldsymbol{\varepsilon} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t), \quad (2)$$

where A_0 is proportional to the amplitude of the incident electric field. The wave vector **k** describes the propagation direction with a magnitude $k = |\mathbf{k}| = \omega/c$. The propagation direction is perpendicular to the polarization vector $\boldsymbol{\varepsilon}$. We can describe the electric field in terms of this vector potential

$$\mathbf{E}(\mathbf{r}, t) = -\frac{1}{c} \frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} = A_0 k \boldsymbol{\varepsilon} \sin(\mathbf{k} \cdot \mathbf{r} - \omega t). \quad (3)$$

The Hamiltonian in Eq. (1) can be separated into a portion independent of the incident field and the perturbing operator,

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t), \quad (4)$$

where

$$\hat{V}(t) = -\frac{e}{m_e c} \sum_i \mathbf{A}(\mathbf{r}_i, t) \cdot \hat{\mathbf{p}}_i. \quad (5)$$

The strength of the incident field is assumed to be weak and the quadratic terms in **A** have been neglected. Using the definitions of the vector potential (Eq. (2)), the perturbing

operator becomes

$$\hat{V}(t) = \frac{eA_0}{m_e c} \sum_i \cos(\mathbf{k} \cdot \mathbf{r}_i - \omega t)(\hat{\mathbf{p}}_i \cdot \boldsymbol{\varepsilon}) \quad (6)$$

$$= \hat{V} \exp(-i\omega t) + \hat{V}^* \exp(i\omega t), \quad (7)$$

with the interaction potential defined as

$$\hat{V} = \frac{eA_0}{2m_e c} \sum_i \exp(i\mathbf{k} \cdot \mathbf{r}_i)(\hat{\mathbf{p}}_i \cdot \boldsymbol{\varepsilon}). \quad (8)$$

This potential can be used with Fermi's golden rule to describe the rate of transition between two states

$$\Gamma_{0n}(\omega) = \frac{2\pi}{\hbar} |\langle 0| \hat{V} |n\rangle|^2 \delta(\omega - \omega_{0n}) \quad (9)$$

$$= \frac{\pi A_0^2}{2\hbar c^2} |T_{0n}|^2 \delta(\omega - \omega_{0n}), \quad (10)$$

where T_{0n} is the transition moment between states $|0\rangle$ and $|n\rangle$. Following an integration over all frequencies and the inclusion of additional prefactors, we can arrive at the expression for the dimensionless oscillator strength,

$$f_{0n} = \frac{2m_e}{e^2 E_{0n}} |T_{0n}|^2, \quad (11)$$

where E_{0n} is the transition energy between states $|0\rangle$ and $|n\rangle$. This represents the transition probability between two states relative to a classical electron in a harmonic potential.[18] The experimentally observed absorption intensity is proportional to Eq. (11) and the oscillator strength is often convoluted with a broadening function when results are compared with experimental lineshapes.

B. Multipole expansion

The perturbing operator (Eq. (8)) can be greatly simplified by expanding the plane wave in a Taylor series and truncating at some finite order,

$$\exp(i\mathbf{k} \cdot \mathbf{r}_i) = 1 + i\mathbf{k} \cdot \mathbf{r}_i + \frac{1}{2}(i\mathbf{k} \cdot \mathbf{r}_i)^2 + \cdots. \quad (12)$$

This expansion is commonly truncated at the first term, leading to the well-known EDA. This assumes that the wavelength of the incident field is long compared to the size of the system and that the intensity of the field is constant over the length of the system. Within this approximation, the transition moment is simply the electric dipole (E1) transition moment, expressed in atomic units as

$$T_{0n}^{(E1)} = \sum_i \langle 0| \hat{\mathbf{p}}_i \cdot \boldsymbol{\varepsilon} |n\rangle$$

$$= \boldsymbol{\varepsilon} \cdot \langle 0| \hat{\boldsymbol{\mu}} |n\rangle. \quad (13)$$

For the vast majority of spectroscopic experiments, the molecules are randomly oriented with respect to the incident field. The oscillator strength should therefore be isotropically averaged[20] to account for these random orientations in the ensemble. The isotropically averaged electric dipole oscillator strength (in atomic units) is

$$\langle f_{0n}^{(E1)} \rangle_{\text{iso}} = \frac{2}{3E_{0n}} |\langle 0| \hat{\boldsymbol{\mu}} |n\rangle|^2. \tag{14}$$

This expression is zero-order in the wave vector and is commonly used to describe absorption intensities for low energy absorption spectra. However, the EDA is not always valid when the molecular system is very large or the wavelength of the incident field is very small (e.g., X-ray). Additional terms accounting for variation in the field over the length of the molecule should be included in the description of the transition moment and oscillator strength.[21–23] In this case, the Taylor expansion of the plane wave is commonly truncated after the second term.[4,15] This leads to the magnetic dipole (M1) and electric quadrupole (E2) transition moments

$$T_{0n}^{(M1)} = \frac{i}{2}(\mathbf{k} \times \boldsymbol{\varepsilon}) \cdot \sum_i \langle 0| (\mathbf{r}_i \times \hat{\mathbf{p}}_i) |n\rangle$$

$$= \frac{i}{2}(\mathbf{k} \times \boldsymbol{\varepsilon}) \cdot \langle 0| \hat{\mathbf{m}} |n\rangle, \tag{15}$$

$$T_{0n}^{(E2)} = \frac{i}{2} \sum_{\alpha\beta} \sum_i k_\alpha \varepsilon_\beta \langle 0| r_{i,\alpha}\hat{p}_{i,\beta} + \hat{p}_{i,\alpha}r_{i,\beta} |n\rangle$$

$$= \frac{i}{2} \sum_{\alpha\beta} k_\alpha \varepsilon_\beta \langle 0| \hat{Q}_{\alpha\beta} |n\rangle, \tag{16}$$

where the Greek indices run over Cartesian coordinates. Contributions from the spin operator will be neglected throughout because states with different M_S values will be degenerated and their spin contributions to the magnetic transition moments will cancel out.[5,24]

With this truncation of the Taylor expansion all isotropically averaged cross terms become zero and the two additional contributions to the oscillator strength are

$$\langle f_{0n}^{(M1)} \rangle_{\text{iso}} = \frac{\alpha^2}{6} E_{0n} |\langle 0| \hat{\mathbf{m}} |n\rangle|^2, \tag{17}$$

$$\langle f_{0n}^{(E2)} \rangle_{\text{iso}} = \frac{\alpha^2}{20} E_{0n} \left[\sum_{\alpha\beta} \langle 0| \hat{Q}_{\alpha\beta}|n\rangle^2 - \frac{1}{3}\left(\sum_\alpha \langle 0| \hat{Q}_{\alpha\alpha} |n\rangle \right)^2 \right]. \tag{18}$$

Where α outside the summation is the fine structure constant. While the electric dipole expressions in Eqs. (13) and (14) are both zero-order in the wave vector, truncating the Taylor expansion after the second term leads to transition moments that are first-order in the wave vector and oscillator strength terms that are second-order.

As is often the case when molecular properties are described beyond the lowest nonzero multipole order, the oscillator strength becomes origin-dependent when the $f_{0n}^{(M1)}$ and $f_{0n}^{(E2)}$ terms are included.[6,7] This is obviously problematic because the obtained physical observable is origin-independent. Bernadotte *et al.* have recently shown that this origin dependence is due to inconsistent treatment of the oscillator strength through second-order.[5] The additional second-order contributions to the oscillator strength contain the magnetic quadrupole (M2) and the electronic octupole (E3) transition moments,

$$T_{0n}^{(M2)} = -\frac{1}{6} \sum_{\alpha\beta} \sum_i (\mathbf{k} \times \boldsymbol{\varepsilon})_\alpha k_\beta \langle 0| r_{i,\beta}(\mathbf{r}_i \times \hat{\mathbf{p}}_i)_\alpha$$

$$+ (\mathbf{r}_i \times \hat{\mathbf{p}}_i)_\alpha r_{i,\beta} |n\rangle$$

$$= -\frac{1}{6} \sum_{\alpha\beta} (\mathbf{k} \times \boldsymbol{\varepsilon})_\alpha k_\beta \langle 0| \hat{\mathcal{M}}_{\alpha\beta} |n\rangle, \tag{19}$$

$$T_{0n}^{(E3)} = -\frac{1}{6} \sum_{\alpha\beta\gamma} \sum_i k_\alpha k_\beta \varepsilon_\gamma \langle 0| r_{i,\alpha}r_{i,\beta}\hat{p}_{i,\gamma}$$

$$+ r_{i,\alpha}\hat{p}_{i,\beta}r_{i,\gamma} + \hat{p}_{i,\alpha}r_{i,\beta}r_{i,\gamma} |n\rangle$$

$$= -\frac{1}{6} \sum_{\alpha\beta\gamma} k_\alpha k_\beta \varepsilon_\gamma \langle 0| \hat{O}_{\alpha\beta\gamma} |n\rangle. \tag{20}$$

When the magnitude of the transition moment is squared to derive the oscillator strength (Eq. (11)), there are two cross terms that include the product between these and the E1 transition moment. The isotropically averaged cross terms are

$$\langle f_{0n}^{(M2)} \rangle_{\text{iso}} = \frac{\alpha^2}{9} E_{0n} \sum_{\alpha\beta\gamma} \epsilon_{\alpha\beta\gamma} \langle 0| \hat{\mu}_\beta |n\rangle \langle 0| \hat{\mathcal{M}}_{\gamma\alpha} |n\rangle, \tag{21}$$

$$\langle f_{0n}^{(E3)} \rangle_{\text{iso}} = -\frac{2\alpha^2}{45} E_{0n} \sum_{\alpha\beta} \langle 0| \hat{\mu}_\beta |n\rangle \langle 0| \hat{O}_{\alpha\alpha\beta} |n\rangle, \tag{22}$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor. While all second-order terms are individually origin-dependent, these dependencies cancel out when all terms are included. It has also been shown that the oscillator strength is always origin-independent when treated consistently through a finite order in the wave vector.[5]

The spectra obtained from different expressions for the oscillator strength can be strikingly different,

$$f^{(0)} = \langle f_{0n}^{(E1)} \rangle_{\text{iso}}, \tag{23}$$

$$f^{(E1+E2+M2)} = \langle f_{0n}^{(E1)} \rangle_{\text{iso}} + \langle f_{0n}^{(M1)} \rangle_{\text{iso}} + \langle f_{0n}^{(E2)} \rangle_{\text{iso}}, \tag{24}$$

$$f^{(2)} = \langle f_{0n}^{(E1)} \rangle_{\text{iso}} + \langle f_{0n}^{(M1)} \rangle_{\text{iso}} + \langle f_{0n}^{(E2)} \rangle_{\text{iso}},$$

$$+ \langle f_{0n}^{(M2)} \rangle_{\text{iso}} + \langle f_{0n}^{(E3)} \rangle_{\text{iso}}. \tag{25}$$

The transition probabilities calculated with the zero-order expression (Eq. (23)) will be strictly zero for dipole-forbidden transitions; the EDA cannot describe quadrupole-allowed transitions. Improper treatment of the oscillator strength through second-order (denoted as $f^{(E1+M1+E2)}$ in Eq. (24)) can result in artificial enhancement of transition probabilities and qualitatively wrong spectral shapes that are dependent upon the origin definition. Unlike $f^{(E1+M1+E2)}$, the full second-order expression (Eq. (25)) is origin-independent and retains many of the properties expected of an oscillator strength. While the origin-independent expression may be preferable, it is not completely devoid of problems since it is still a truncated form of the complete, infinite order operator. The failings of the $f^{(E1+M1+E2)}$ expression and some potential problems associated with $f^{(2)}$ are explored in Sec. IV.

C. Different gauges

The electric transition moments in Eqs. (13), (16), and (20) are in their velocity gauge representations. When a complete basis set is used, there are equivalent expressions in

which the operator takes a different form.[19] The relationship between these expressions can be shown for the E1 transition moment using the commutation relationship

$$[r_{i,\alpha}, \hat{H}_0] = \frac{i\hbar}{m_e} \hat{p}_{i,\alpha}. \qquad (26)$$

This relationship can be used with Equation (13) to show that the E1 transition moment can also be written (in atomic units) as

$$T_{0n}^{(E1)} = -i E_{0n} \sum_i \langle 0| \mathbf{r}_i \cdot \boldsymbol{\varepsilon} |n\rangle . \qquad (27)$$

Similar commutation relationships (see Appendix A of Ref. 5) can be used to show that

$$T_{0n}^{(E2)} = \frac{E_{0n}}{2} \sum_{\alpha\beta} \sum_i k_\alpha \varepsilon_\beta \langle 0| r_{i,\alpha} r_{i,\beta} |n\rangle , \qquad (28)$$

$$T_{0n}^{(E3)} = i\frac{E_{0n}}{6} \sum_{\alpha\beta\gamma} \sum_i k_\alpha k_\beta \varepsilon_\gamma \langle 0| r_{i,\alpha} r_{i,\beta} r_{i,\gamma} |n\rangle , \qquad (29)$$

when a complete basis set is used. These expressions are referred to as the length gauge representations of the electric transition moments. There are also corresponding length gauge expressions for the oscillator strength that are equivalent to those in the velocity gauge when a complete basis set is used.

It is important to note that when the basis set is incomplete, $f^{(2)}$ is only origin-independent in the velocity gauge. The origin dependence of the magnetic multipole integrals can be represented in terms of lower order magnetic multipoles and velocity gauge electric multipoles. This can be shown by shifting the molecular origin from $\mathbf{O}$ to $\mathbf{O} + \mathbf{a}$,

$$\langle 0| \hat{m}_\alpha(\mathbf{O}+\mathbf{a}) |n\rangle = \langle 0| \hat{m}_\alpha(\mathbf{O}) |n\rangle - \epsilon_{\alpha\beta\gamma} a_\beta \langle 0| \hat{\mu}_\gamma |n\rangle , \qquad (30)$$

$$\begin{aligned} \langle 0| \hat{\mathcal{M}}_{\alpha\beta}(\mathbf{O}+\mathbf{a}) |n\rangle &= \langle 0| \hat{\mathcal{M}}_{\alpha\beta}(\mathbf{O}) |n\rangle - 3 a_\beta \langle 0| \hat{m}_\alpha(\mathbf{O}) |n\rangle \\ &\quad + \delta_{\alpha\beta} (\mathbf{a} \cdot \langle 0| \hat{\mathbf{m}}(\mathbf{O}) |n\rangle) \\ &\quad + \sum_{\gamma\delta} \epsilon_{\alpha\gamma\delta} [2 a_\beta a_\gamma \langle 0| \hat{\mu}_\gamma |n\rangle \\ &\quad - a_\gamma \langle 0| \hat{Q}_{\beta\delta}(\mathbf{O}) |n\rangle] . \end{aligned} \qquad (31)$$

For a detailed derivation, see the supplementary material of Ref. 5. For problems of chemical relevance, it is usually impractical to use a complete basis set. In order to maintain origin independence, all second-order contributions to the oscillator strength presented in this work will be calculated in the velocity gauge.

The zero-order expression for the oscillator strength is origin-independent in both the length and velocity gauges and there has been considerable debate over the appropriate gauge to describe transition probabilities.[25–28] Recent work on propagating the electronic density in time while coupled to the electric field through the electric dipole has shown that the length gauge representation tends to be more numerically stable.[19] This is also the gauge most commonly used and is employed for the $f^{(0)}$ results presented in this work. This mixed gauge representation is consistent with that presented by Bernadotte *et al.* in Ref. 5.

III. COMPUTATIONAL DETAILS

The multipole expansion may be used to describe transition probabilities for any quantum mechanical method able to describe electronic excited states. We will use linear response TDDFT for our discussion. A formal response theory is appealing because it allows us to discuss the Thomas-Reiche-Kuhn sum rule.[29–31] This sum rule does not hold for approximate response methods such as Configuration Interaction Singles (CIS)[32] and the Tamm-Dancoff approximation (TDA).[33,34]

The X-ray absorption energies and oscillator strengths are calculated using energy-specific TDDFT (ES-TDDFT)[15,16] in a development version of the Gaussian software package.[35] To first order, the density matrix response to the perturbation can be written in terms of excitation and de-excitation amplitudes, which are found by solving the TDDFT equations,

$$\rho(x, x') = \sum_{ia} (X_{ia} \varphi_a(x) \varphi_i(x') + Y_{ia} \varphi_i(x) \varphi_a(x')), \qquad (32)$$

where the i and a subscripts refer to occupied and virtual orbitals, respectively. The transition moments between electronic states are calculated as the trace of the transition density with multipole integrals in the MO basis. The $[\mathbf{X} + \mathbf{Y}]$ or $[\mathbf{X} - \mathbf{Y}]$ density is used depending on if the operator is Hermitian or anti-Hermitian, respectively. For example, the length gauge E1 transition moment is calculated as

$$\langle 0| \sum_k r_{k,\alpha} |n\rangle = \sqrt{2} \sum_{ia} [X_{ia}^n + Y_{ai}^n] \langle \psi_i| \sum_k r_{k,\alpha} |\psi_a\rangle , \qquad (33)$$

where ψ_p are molecular orbitals. For all calculations presented herein, geometries are optimized with the PBE1PBE functional (also known as PBE0)[36,37] and the 6-31+G(d) basis set.[38–42]

IV. RESULTS AND DISCUSSION

A. Thomas-Reiche-Kuhn sum rule

Oscillator strengths obtained from Time-Dependent Hartree-Fock (TDHF)[43] and TDDFT[44] obey the Thomas-Reiche-Kuhn sum rule.[29–31]

$$\sum_i f_{ij} = N. \qquad (34)$$

This says that the sum of all oscillator strengths from a particular state to all others will equal the number of electrons in the system. When the infinite order expression for the transition moment is used, the oscillator strength is origin-independent and obeys this sum rule in any coordinate system definition. However, if the oscillator strength is treated incompletely at some finite order, the oscillator strength is not guaranteed to satisfy this sum rule. This behavior can be illustrated (in Fig. 1) using the $f^{(0)}$, $f^{(E1+M1+E2)}$, and $f^{(2)}$ expressions to model excitations of molecular hydrogen calculated with the PBE1PBE functional and the daug-cc-pVTZ basis set.[45–47] The system is originally oriented along the z-axis with the origin placed at the center of the molecular bond. The origin is then displaced along the x-axis and the sum rule evaluated at all definitions of the origin.
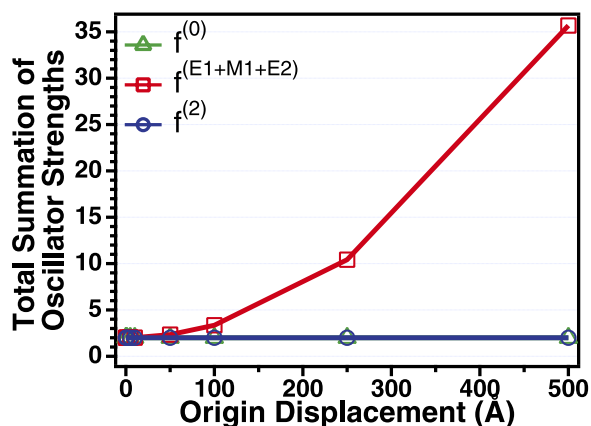
FIG. 1. The sum of oscillator strengths from 68 excitations of H_2 calculated at the PBE1PBE/daug-cc-pVTZ level of theory. Three different oscillator strength expressions are used: $f^{(0)}$, $f^{(E1+M1+E2)}$, and $f^{(2)}$. Note that the $f^{(0)}$ and $f^{(2)}$ plots overlap almost exactly.

The EDA is, of course, more than sufficient to describe transition probabilities for molecular hydrogen. The zero-order expression is origin-independent and the sum rule is satisfied at all definitions of the origin. When the second-order oscillator strength is treated incompletely, the summation total is widely inflated as the origin is moved far away from the molecular system, rising to >35 when the origin is displaced by 500 Å. To the best of our knowledge, this behavior of the $f^{(E1+M1+E2)}$ expression has not yet been reported in the literature. This behavior is corrected, however, when the cross terms are included and the complete second-order expression is used. The sum rule is then satisfied at any definition of the origin, as it should be.

This behavior alone is not sufficient to say that $f^{(E1+M1+E2)}$ should not be used because there is no reason to place the molecular origin outside of the molecular system. Those definitions of the origin do not allow one to take advantage of molecular symmetry and reduce computational cost. Also, methods such as CIS and TDA do not satisfy this sum rule and are used to successfully model experimental spectra nonetheless. We will next turn our attention to more reasonable origin definitions contained within the molecular system and show how these still have a large effect on the resulting spectrum when using $f^{(E1+M1+E2)}$.

B. Lineshape variation

The $f^{(E1+M1+E2)}$ expression can result in very different spectra for different definitions of the origin. We can show this by modeling a derivative of the low bandgap polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCP-DTBT) where the alkyl chains have been replaced with methyl groups (Fig. 2). The nitrogen and sulfur K-edges of this system have been previously investigated both experimentally and theoretically.[48,49] We will focus on the sulfur K-edge transitions as the wavelength is about 0.5 nm and a single subunit of this polymer is >1 nm, making it a likely case where the EDA would break down.

Spectra using the origin-independent $f^{(0)}$ and $f^{(2)}$ expressions and the origin-dependent $f^{(E1+M1+E2)}$ expression
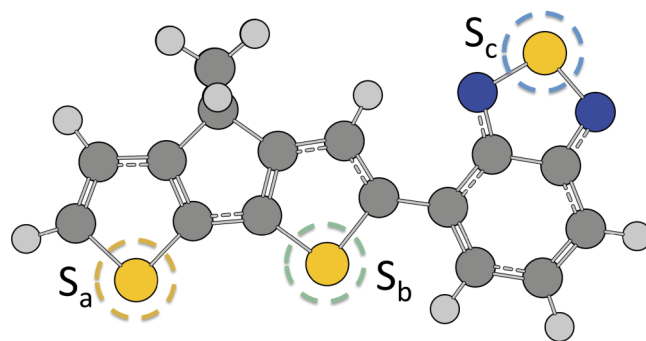

FIG. 2. A single subunit of the PCPDTBT polymer where the alkyl chains have been replaced with methyl groups. The different sulfur atoms are denoted as S_{a-c} in order to identify different definitions of the origin to compare with their respective spectra in Fig. 3.

are plotted in Fig. 3(a). We have placed the origin at the center of mass (COM) of the system and on each sulfur atom (denoted as S_{a-c} in Fig. 2) to show the variation in the origin-dependent expression. All transitions are broadened with Lorentzian functions with FWHM of 0.35 eV consistent with the core-hole lifetime for sulfur K-edge transitions.[50,51]

All oscillator strengths calculated with $f^{(E1+M1+E2)}$ are far greater than those calculated with $f^{(0)}$ or $f^{(2)}$ (Fig. 3(a)). They also vary dramatically for different definitions of the origin. The zero- and second-order spectra are virtually identical as the cross terms largely cancel out contributions from Eqs. (17) and (18). This may seem counterintuitive because the size of this system is more than twice the
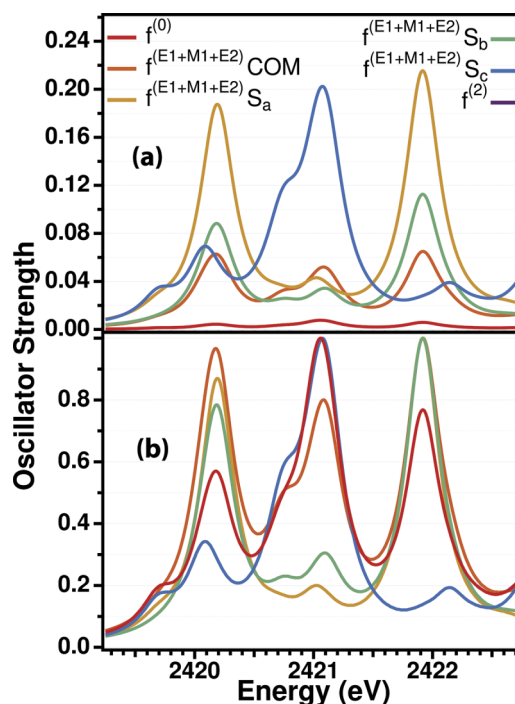

FIG. 3. (a) Unnormalized and (b) normalized sulfur K-edge spectra of the PCPDTBT derivative in Fig. 2. The $f^{(0)}$ and $f^{(2)}$ definitions of the oscillator strength as well as the $f^{(E1+M1+E2)}$ expression with four different definitions of the origin are included. The origin is placed at the COM and on each sulfur atom denoted as S_{a-c}. Note that the $f^{(0)}$ and $f^{(2)}$ spectra overlap almost exactly. The individual oscillator strengths are left out for clarity.

wavelength of the exciting electromagnetic field and the EDA is expected to break down. List *et al.* have observed similar behavior for *trans*-polyenes of varying lengths.[8] The modest effect of higher-order contributions was attributed to the localized nature of the initial state which confines the transition density around the core hole. The PCPDTBT transitions are all localized around the excited atom, which explains the very small change when going beyond the EDA. Further, the largest possible error due to the EDA is about 20% so we would only ever expect a small effect for these dipole-allowed transitions.[8]

When comparing to experimental results, modeled spectra are rescaled in order to compare with the experimental intensities. With this in mind, it is important to consider how the different oscillator strength expressions can change the relative peak intensities and overall spectral features and not just the overall intensity. Figure 3(b) contains normalized spectra such that the strongest transition is set to unity. There are three dominant transitions with the middle transition often having a shoulder slightly lower in energy. For the $f^{(E1+M1+E2)}$ expression, when the origin is place on S_a or S_b, the middle transition is strongly dampened and when the origin is placed on S_c, this feature is strongly enhanced relative to the other peaks. This origin-dependent enhancement of features can be rationalized in terms of where the excitation is localized on the system.

The core hole of the dominant transitions for the features around 2420 and 2422 eV is localized on S_c. The dominant transition contributing to the feature around 2421 eV has the core hole localized on S_a. When the origin is placed on the excited sulfur atom, the oscillator strength calculated with $f^{(E1+M1+E2)}$ is much closer to that calculated with $f^{(0)}$ or $f^{(2)}$ (evident in Fig. 3(a)). The reverse is also true: when the origin is placed far from the excited atom, the oscillator strength calculated with $f^{(E1+M1+E2)}$ is artificially enhanced relative to the correct value. This behavior is consistent with that seen by Neese and co-workers and one of the arguments for placing the origin within the transition density so the Taylor series expansion of the plane wave converges more quickly.[4] With the origin placed at the COM, the three features all have comparable intensities, although the relative magnitude of the three features is still not consistent with the $f^{(0)}$ and $f^{(2)}$ expressions. This enhancement and dampening of features could be mitigated by changing the molecular origin to be within the transition density of each excitation although this would be rather tedious as well as computationally inefficient.

An incomplete treatment of the oscillator strength through second-order can result in variable spectral shapes dependent upon the location of the origin and the localization of the transition densities. This can result in the dampening of important features and the enhancement of features that are insignificant experimentally. This is particularly troubling when $f^{(E1+M1+E2)}$ is used because spectral features may be misassigned and the experiment interpreted incorrectly if too much confidence is placed in the theoretical model. Although much of this can be accounted for by shifting the origin for each transition to be within the transition density. In short, the $f^{(E1+M1+E2)}$ expression is not an appropriate way to model the oscillator strength unless particular care is taken when

defining the molecular origin. The $f^{(2)}$ expression, on the other hand, does not require this type of consideration and is always independent of the coordinate system.

C. Negative oscillator strengths

The oscillator strength is a measure of transition probability and should always be positive for absorption processes, although it can be negative for emission,[17] by virtue of the fact that the difference between the energy of the final and initial states is negative, while the sum-rule is still satisfied. The $f^{(0)}$ and $f^{(E1+M1+E2)}$ expressions are always positive because they arise from a truncation of the Taylor expansion of the plane wave at some finite order. The transition moments are evaluated with this truncation and their magnitude is squared keeping all nonzero terms. The full second-order expression, however, comes from keeping all terms through second-order after the magnitude of the transition moment has been squared. The resulting cross terms make it possible that the oscillator strength can become negative.

$TiCl_4$ has been studied experimentally and theoretically by several different groups and is often used to illustrate the ability of a TDDFT based method to model X-ray excitations.[4,5,15,52–54] It is a tetrahedral coordinated system of T_d symmetry, so the five Ti d orbitals are split into two sets of two and three orbitals that transform as the e and t_2 irreducible representations, respectively. The experimental pre-edge peak is a rather broad feature requiring two peaks to fit, which are assigned as excitations to the e and t_2 sets of Ti d orbitals. We will focus on excitations to the e set of orbitals.

There are eight different transitions to the e set of Ti d orbitals that are around ~2763 eV when calculated at the PBE1PBE/6-31+G(d) level of theory (Table I). The first six excitations are dominated by transitions from the t_2 Cl 1s orbitals and the final two are dominated by transitions from the a_1 orbital. The excitations from the t_2 orbitals are further separated into two sets of triply degenerate transitions, one of which is dipole-allowed. These dipole-allowed transitions have negative oscillator strengths when the second-order expression is used. The second-order cross terms include the electric dipole and either the magnetic quadrupole or the electric octupole. These second-order terms can either be positive or negative depending on the signs

TABLE I. Oscillator strengths for Cl 1s → Ti 3d transitions calculated at the PBE1PBE/6-31+G(d) level of theory. The excitation energies are shifted by −2763 eV.

Symmetry	Energy (meV)	$10^3 f^{(0)}$	$10^3 f^{(E1+M1+E2)}$	$10^3 f^{(2)}$
T_1	4.474	0.00	5.54	5.54
T_1	4.474	0.00	5.54	5.54
T_1	4.474	0.00	5.54	5.54
T_2	4.482	2.48	3.59	−5.28
T_2	4.482	2.48	3.59	−5.28
T_2	4.482	2.48	3.59	−5.28
E	4.515	0.00	3.32	3.32
E	4.515	0.00	3.32	3.32

of these transition moments and will only be nonzero for dipole-allowed transitions. This means that the only instance where the second-order oscillator strength can be negative is when the E1 transition moment is nonzero. Unfortunately, the addition of the cross-terms between the electric dipole and the electric octupole and magnetic quadrupole terms provides an origin-independent oscillator strength, but the resulting expression is no longer a perfect square. To the best of our knowledge, the possibility of negative oscillator strengths with the $f^{(2)}$ expression has not yet been discussed in the literature.

From an experimental point of view, the intrinsic broadening of these excitations is so large that they cannot be individually resolved; therefore, no comparison can be made with the calculated intensities for each transition. However, the fact that the computed oscillator strength is negative may be considered a diagnostic for the need to include even higher order multipole contributions in the model, since the exact (untruncated) quantity is assured to be positive for absorption processes. In fact, as can be seen from Table I, the effect of the second-order terms is of the same order of magnitude as the electric dipole contribution for the T_2 transition. It should also be pointed out that the TRK sum rule should still be satisfied; therefore, the positive contributions from the second-order terms in other transitions will compensate for the negative ones when the sum is performed.

V. CONCLUSION

The origin-dependent $f^{(E1+M1+E2)}$ expression is commonly used to describe X-ray absorption spectra when the EDA is expected to breakdown. We have shown that this expression is not guaranteed to satisfy the Thomas-Reiche-Kuhn sum rule and can often result in different spectral shapes dependent upon the origin definition. This is true even in cases where the EDA is still valid as different definitions of the origin can artificially enhance higher order terms in the oscillator strength expression. Spectra obtained using this expression are not likely to be reliable unless particular care is taken when assigning the molecular origin for each calculated transition. Full treatment of the oscillator strength through second-order removes many of these strange behaviors; the sum rule is satisfied and the spectral lineshape is consistent at all definitions of the origin. However, the $f^{(2)}$ expression can result in negative oscillator strengths for dipole-allowed transitions. This has been observed for several Cl K-edge transitions of $TiCl_4$, but it is not yet clear how common this behavior is. Having negative oscillator strengths would prevent one from making spectral assignments and is a diagnostic for the need to use a higher order expansion or the untruncated form of the operator. When the transition moment and oscillator strength are treated through infinite order, these undesirable properties are no longer present. It seems that either the electric dipole approximation or the infinite order oscillator strength should be used. Any other truncation of the plane wave Taylor expansion can lead to strange and unphysical behaviors that can effect the way spectral features are assigned.

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