Magnetic circular dichroism in real-time time-dependent density functional theory

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Abstract

We apply the adiabatic time-dependent density functional theory to magnetic circular dichroism (MCD) spectra using the real-space, real-time computational method. The standard formulas for the MCD response and its \( A \) and \( B \) terms are derived from the observables in the time-dependent wave function. We find real time method is well suited for calculating the overall spectrum, particularly at higher excitation energies where individual excited states are numerous and overlapping. The MCD sum rules are derived and interpreted in the real-time formalism; we find that they are very useful for normalization purposes and assessing the accuracy of the theory. The method is applied to MCD spectrum of \( C_{60} \) using the adiabatic energy functional from the local density approximation. The theory correctly predicts the signs of the \( A \) and \( B \) terms for the lowest allowed excitations. However, the magnitudes of the terms only show qualitative agreement with experiment.
I. INTRODUCTION

Magnetic circular dichroism (MCD) is an important spectroscopic observable useful for characterizing the electronic structure of molecules [1] and condensed matter systems [2]. The theory of the MCD response is usually given as a third-order perturbation in a basis that diagonalizes the zero-field Hamiltonian. This formulation, called the sum-over-states method, requires a considerable computational effort to construct the states and perform the summations. There have been recent attempts to simplify the calculation by using eigenstates of the Hamiltonian in the presence of the magnetic field [3, 4], but one still requires a sum over transition densities. We propose here a completely different formalism based on the solution of time-dependent equations of motion and present a formalism for $A$ and $B$ terms of the MCD. We find that the formalism is a practical one when applied in the framework of time-dependent density functional theory (TDDFT). In fact, the TDDFT has already been used successfully to calculate MCD in molecules [5–7]. A separate problem in the theory of MCD is the choice of a basis set to construct the electron orbital wave functions. The MCD puts higher demands on the orbital representation to satisfy completeness and gauge invariance. In our treatment, we represent the orbital wave functions on a spatial mesh rather than with atom-centered basis set. The calculated matrix elements are automatically gauge-invariant and one also avoids the inconsistencies that cause sum rules to be violated.

We mention that the real-time TDDFT has been applied to many observables related to electron dynamics [8–10]. Specific applications include the molecular absorption spectrum in the continuum [11], hyperpolarizabilities [12–14], the dielectric function [15], and chiral dichroism [16]. The real-time method has also been applied to phenomena associated with high fields. In the presence of high fields, there is hardly any alternative theory available, at least at the ab initio DFT level. Applications include nonlinear electron dynamics in metallic clusters [17], high harmonic generation [18], Coulomb explosion [19, 20] dielectric breakdown [21], and coherent phonon generation [22].

The organization of this article is as follows. In Section II we define the time-dependent quantities that are computed and derive the formulas for extracting the observables related to MCD. We also review the sum rules satisfied by the MCD response in that Section. In Section III we provide some of the numerical details in carrying out the MCD calculations. Following that, in Section IV, we apply the theory to the $C_{60}$ molecule. Due to its high
symmetry, the \( C_{60} \) molecule can exhibit both \( A \) and \( B \) terms of MCD. The lowest electronic excitations of this molecule are the \( \pi - \pi^* \) character; for the measured transitions we find the correct signs for the calculated \( A \) and \( B \) terms. The theory is in qualitative agreement also with magnitude of the \( B \) term of the lowest transition. However, the present theory does not reproduce well the other transitions and the magnitude of the \( A \) term.

II. THEORY

A. Definitions for MCD response function

We consider a molecule under a static magnetic field \( B \) in \( \gamma \) direction. The electronic Hamiltonian is written as

\[
H = H_0 + \mu_B B L_\gamma,
\]

where \( H_0 \) is the Hamiltonian in the absence of the magnetic field, \( L_\gamma \) is the angular momentum operator, and \( \mu_B = e/2mc \) is the Bohr magneton. We take a convention of \( e > 0 \) and \( \hbar = 1 \). We denote the ground and excited states under the static magnetic field \( B \) as

\[
H \Phi_n = E_n \Phi_n.
\]

We denote the dipole operator as \( \vec{\mu} = -e \sum \vec{r}_i \) where \( \vec{r}_i \) are electron coordinates. We define the circularly polarized dipole operators with the normalization convention \( \mu^{(\gamma)}_{\pm} = (\mu_\alpha \pm i \mu_\beta)/\sqrt{2} \), where \((\alpha\beta\gamma)\) is a cyclic permutation of \((xyz)\).

In MCD, the basic object of study is the difference in dipole absorption strength functions for light of opposite circular polarization in a weak magnetic field. The MCD response may be defined by the strength function

\[
R_{\text{MCD}}(E) = \frac{1}{3\mu_B B} \sum_n \sum_\gamma \delta(E - E_{n0}) \left\{ |\langle \Phi_0 | \mu^{(-)}_{\gamma} | \Phi_n \rangle|^2 - |\langle \Phi_0 | \mu^{(\gamma)}_{\pm} | \Phi_n \rangle|^2 \right\},
\]

where \( E_{n0} \) is the excitation energy of state \( n \), \( E_{n0} = E_n - E_0 \). The beam direction coincides with the magnetic field direction along an axis labeled by \( \gamma \). It is convenient to express the strength function in a Cartesian basis using the antisymmetric tensor \( \epsilon_{\alpha\beta\gamma} \),

\[
R_{\text{MCD}}(E) = -\frac{1}{3\mu_B B} \sum_{\alpha\beta\gamma} \epsilon_{\alpha\beta\gamma} \sum_n \delta(E - E_{n0}) \text{Im} \left\{ \langle \Phi_0 | \mu_{\alpha} | \Phi_n \rangle \langle \Phi_n | \mu_{\beta} | \Phi_0 \rangle \right\},
\]

where the magnetic field is applied to \( \gamma \) direction.
To assess the quality of the theory, it is also useful to calculate the ordinary dipole response. We define the dipole response \( R_D(E) \)

\[
R_D(E) = \frac{1}{3} \sum_n \sum_{\alpha} \delta(E - E_{n0}) |\langle \Phi_0|\mu_{\alpha}|\Phi_n \rangle|^2,
\]

(5)

This is related to the oscillator strength distribution by

\[
\frac{df}{dE} = \frac{2mE_{n0}}{e^2} R_D(E).
\]

(6)

Below the ionization threshold, electronic states are discrete. In this energy region, the MCD strength function is often written as

\[
R_{\text{MCD}}(E) = \sum_n \left\{ A_n \left( - \frac{d}{dE} F_n(E - E_{n0}^{(B=0)}) \right) + B_n F_n(E - E_{n0}^{(B=0)}) \right\},
\]

(7)

where \( F_n(E) \) is the spectral shape of the \( n \)-th state normalized as \( \int F_n(E) dE = 1 \). The zero-field excitation energy is expressed as \( E_{n0}^{(B=0)} \). There appear both \( A \) and \( B \) terms for molecules with degeneracy in either ground or excited states, while only \( B \) term appears for molecules without degeneracy in any states. Integrating the MCD response function over an excitation energy around \( E_{n0}^{(B=0)} \), we have

\[
A_n = \int_{E_{n0} - \epsilon}^{E_{n0} + \epsilon} dE (E - E_{n0}^{(B=0)}) R_{\text{MCD}}(E),
\]

(8)

and

\[
B_n = \int_{E_{n0} - \epsilon}^{E_{n0} + \epsilon} dE R_{\text{MCD}}(E),
\]

(9)

where \( \epsilon \) is a small energy interval.

Employing the perturbation theory, these terms may be expressed in terms of the energy and the wave functions in the absence of the magnetic field. For \( A \), we have

\[
A_n = -\frac{1}{3} \sum_{\alpha\beta\gamma} \epsilon_{\alpha\beta\gamma} \sum_{st} \left\{ (L_\gamma)_{nt,nt} - (L_\gamma)_{0s,0s} \right\} \text{Im} \langle \Phi_{0s}|\mu_{\alpha}^{(\gamma)}|\Phi_{nt}\rangle \langle \Phi_{nt}|\mu_{\beta}^{(\gamma)}|\Phi_{0s}\rangle,
\]

(10)

where \( s \) and \( t \) distinguishes degenerate states of ground and excited states, respectively. The basis which diagonalize \( L_\gamma \) is assumed. For \( B \), we have

\[
B_n = \frac{2}{3} \text{Im} \sum_{\alpha\beta\gamma} \epsilon_{\alpha\beta\gamma} \sum_m \left\{ \frac{1}{E_{m0}} \langle \Phi_m|L_\gamma|\Phi_0\rangle \langle \Phi_0|\mu_{\alpha}|\Phi_n\rangle \langle \Phi_n|\mu_{\beta}|\Phi_m\rangle + \frac{1}{E_{mn}} \langle \Phi_n|L_\gamma|\Phi_m\rangle \langle \Phi_0|\mu_{\alpha}|\Phi_n\rangle \langle \Phi_m|\mu_{\beta}|\Phi_0\rangle \right\}.
\]

(11)
Similarly, we define the ordinary dipole strength as

\[ \mathcal{D}_n = \int_{E_n - \epsilon}^{E_n + \epsilon} dE R_D(E) = \frac{1}{3} \sum_\alpha |\langle \Phi_0 | \mu_\alpha | \Phi_n \rangle|^2. \] (12)

It is related to the oscillator strength \( f_n \) as

\[ f_n = \frac{2}{m} E_n \mathcal{D}_n / e^2. \]

Finally, with our definition of the MCD response, the \( B \) coefficient is related to the ratio of the MCD extinction coefficient \( \Delta \epsilon \) to the ordinary extinction coefficient \( \epsilon \) by the formula

\[ \frac{\Delta \epsilon}{\epsilon} = \frac{2 m \mu_B B E_n B_n}{e^2 f_n} \] (13)

B. Real time formulation

The response associated with any pair of operators, \( \mathcal{O}_1 \) and \( \mathcal{O}_2 \), may be calculated in the real time domain starting from the ground state wave function \( \Phi_0 \). One first applies an impulsive perturbation \( \lambda \mathcal{O}_1 \) to obtain an initial wave function \( \Psi(t = 0_+) \). This is then evolved in time with the exponentiated Hamiltonian operator,

\[ \Psi(t) = e^{-iHt} e^{i\lambda \mathcal{O}_1} \Phi_0. \] (14)

The real-time response \( S_{21}(t) \) is given by the expectation value of the operator \( \mathcal{O}_2 \) in that state,

\[ S_{21}(t) = \langle \Psi(t) | \mathcal{O}_2 | \Psi(t) \rangle. \] (15)

The linear response is evaluated by treating \( \lambda \) as a small parameter and taking the derivative \( dS_{21}(t)/d\lambda \) at \( \lambda = 0 \). Depending on the operators \( \mathcal{O}_1 \) and \( \mathcal{O}_2 \), the strength function \( R_{21} \) is obtained as the imaginary or real part of the Fourier transform of linear response \( dS_{21}(t)/d\lambda |_{\lambda=0} \) on the time interval \([0, +\infty)\).

This general formulation of the linear response applies to the MCD strength function Eq. (4) taking the operators to be \( \mathcal{O}_1 = \mu_\beta \) and \( \mathcal{O}_2 = \mu_\alpha \). The wave function is set up at \( t = 0 \) as \( \Psi_{k\beta}(t = 0_+) = e^{i k \mu_\beta} \Phi_0 \) and the real-time response \( S_{\alpha\beta}^{(\gamma)}(t) \) is given by

\[ S_{\alpha\beta}^{(\gamma)}(t) = \langle \Psi_{k\beta}(t) | \mu_\alpha | \Psi_{k\beta}(t) \rangle, \] (16)

where \( (\gamma) \) in \( S_{\alpha\beta}^{(\gamma)} \) is included to remember that a static magnetic field is applied to \( \gamma \) direction throughout the time evolution. Expanding the perturbing operator \( e^{i k \mu_\beta} \) in powers of \( k \), we...
have
\[ S^{(\gamma)}_{\alpha\beta}(t) = ik \left\{ \langle \Phi_0 | \mu_\alpha | \Phi_n \rangle \langle \Phi_0 | \mu_\beta | \Phi_0 \rangle - \langle \Phi_0 | \mu_\beta e^{i(H-E_0)t} | \mu_\alpha | \Phi_0 \rangle \right\}. \]
\[ = ik \sum_n \langle \Phi_0 | \mu_\alpha | \Phi_n \rangle \langle \Phi_n | \mu_\beta | \Phi_0 \rangle e^{-iE_n t} - ik \sum_n \langle \Phi_0 | \mu_\beta | \Phi_n \rangle \langle \Phi_n | \mu_\alpha | \Phi_0 \rangle e^{iE_n t}. \] (17)

In the last formula, we have expressed the time-evolution operator in terms of the energy eigenstates of the system. We next separate out the time-even and time-odd parts of the response, writing it as
\[ S^{(\gamma)}_{\alpha\beta}(t) = -2k \sum_n \text{Im} \left\{ \langle \Phi_0 | \mu_\alpha | \Phi_n \rangle \langle \Phi_n | \mu_\beta | \Phi_0 \rangle \right\} \cos E_n t + 2k \sum_n \text{Re} \left\{ \langle \Phi_0 | \mu_\alpha | \Phi_n \rangle \langle \Phi_n | \mu_\beta | \Phi_0 \rangle \right\} \sin E_n t. \] (18)

The combination \( S^{(\gamma)}_{\alpha\beta} - S^{(\gamma)}_{\beta\alpha} = -4k \sum_n \text{Im} \left\{ \langle \Phi_0 | \mu_\alpha | \Phi_n \rangle \langle \Phi_n | \mu_\beta | \Phi_0 \rangle \right\} \cos E_n t \)
isolates the first term with the cosine dependence on time. We obtain an expression proportional to the MCD response by taking its cosine Fourier transform,
\[ -\frac{1}{2\pi k} \int_0^\infty dt \cos Et \left\{ S^{(\gamma)}_{\alpha\beta} - S^{(\gamma)}_{\beta\alpha} \right\} = \sum_n \text{Im} \left\{ \langle \Phi_0 | \mu_\alpha | \Phi_n \rangle \langle \Phi_n | \mu_\beta | \Phi_0 \rangle \right\} \delta(E - E_n 0). \] (19)

The MCD strength function with the proper prefactor is given by the integral over the real-time response as
\[ R_{\text{MCD}}(E) = \frac{1}{6\pi \mu Bk} \sum_{\alpha\beta\gamma} \epsilon_{\alpha\beta\gamma} \int_0^\infty dt \cos Et \left\{ S^{(\gamma)}_{\alpha\beta} - S^{(\gamma)}_{\beta\alpha} \right\}. \] (20)

For the molecules we treat here, we can choose coordinate systems such that the off-diagonal response is antisymmetric, \( S^{(\gamma)}_{\alpha\beta}(t) = -S^{(\gamma)}_{\beta\alpha}(t) \). Then the second term in Eq. (18) is identically zero and Eq. (20) reduces to
\[ R_{\text{MCD}}(E) = \frac{2}{3\pi \mu Bk} \int_0^\infty dt \cos Et \left\{ S^{(z)}_{2y}(t) + S^{(z)}_{y2}(t) + S^{(y)}_{z2}(t) \right\}. \] (21)

This is our main result that will be applied to calculate the MCD.

For most if not all MCD spectra, the sign of \( R_{\text{MCD}}(E) \) on the infrared side of the lowest optical excitation is negative. We shall call this the “normal” sign.

The ordinary dipole response \( R_D(E) \) may also be computed in the formalism as Fourier sine transform,
\[ R_D(E) = \frac{1}{3\pi k} \sum_\alpha \int_0^\infty dt \sin Et S^{(\gamma)}_{\alpha\alpha}(t). \] (22)

Note that this can easily be evaluated at the same time as \( R_{\text{MCD}}(E) \) because the same time-dependent wave function is used in both.
C. Sum rules

The real-time formalism is very convenient for evaluating and verifying energy-weighted sum rules. In particular, the MCD response satisfies a quadratic sum rule that depends only on the magnetic field strength and the number of electrons [23]. The connection to the time-dependent response may be easily derived by expanding $S_{\alpha\beta}(\gamma)$ as a power series in time $t$,

$$S_{\alpha\beta}(\gamma)(t) \simeq s_0 + s_2 t^2 + \cdots. \tag{23}$$

Only even powers of $t$ are present in the series expansion, due to the suppression of the second term in Eq. (18). The coefficients $s_0$ and $s_2$ can be readily expressed as commutators of the $\mu$ operators and the Hamiltonian and evaluated analytically. One finds

$$s_0 = -2 k \text{Im} \sum_n \{ \langle \Phi_0 | \mu_\alpha | \Phi_n \rangle \langle \Phi_n | \mu_\beta | \Phi_0 \rangle \} = i k \langle \Phi_0 | [\mu_\alpha, \mu_\beta] | \Phi_0 \rangle = 0, \tag{24}$$

and

$$s_2 = k \text{Im} \sum_n \{ \langle \Phi_0 | \mu_\alpha | \Phi_n \rangle \langle \Phi_n | \mu_\beta | \Phi_0 \rangle \} E_n^2 = -\frac{ik}{2} \langle \Phi_0 | [\mu_\alpha, [H, \mu_\beta]] | \Phi_0 \rangle = \pm \frac{e^3 B k}{2m^2 c} N_e \tag{25}$$

where $N_e$ is the number of electrons and the sign reflects the order of $(\alpha\beta\gamma)$. These formulas can be expressed as integrals over the MCD strength function

$$I_0 = \int_0^\infty dE R_{\text{MCD}}(E) = 0 \tag{26}$$

and

$$I_2 = \int_0^\infty dE E^2 R_{\text{MCD}}(E) = \frac{2e^2}{m} N_e. \tag{27}$$

The $I_2$ sum rule has a simple physical interpretation. Consider the real-time response associated with $S_{xy}^{(\gamma)}$. The impulsive exciting potential $ek\gamma \delta(t)$ gives the electrons an average momentum equal to $-ek\hat{y}$, the integral of the force over time. The corresponding velocity, $\vec{v} = -ek\hat{y}/m$, is subject to a magnetic force $-e\vec{v} \times \vec{B}/c$ which is in the $x$ direction for our geometry. The corresponding acceleration is $a = e^2 B k \hat{x}/m^2 c$. Thus the $x$-component of the dipole moment increases quadratically with time according to the acceleration formula

$$\langle -ex(t) \rangle = \frac{1}{2} at^2 = \frac{N_e e^3 B k}{2m^2 c} t^2, \tag{28}$$

in agreement with Eq. (23) and (25).
In the results of the calculations given below, we will also show the performance of the theory with respect to the \( f \)-sum rule. In terms of the response \( R_D(E) \), we define the quantity
\[
f_E = 2m \int_0^E dE' E' R_D(E').
\] (29)

The sum rule is given by
\[
f_+\infty = N_e
\] (30)
where \( N_e \) is the number of electrons. The associated short-time behaviour of the real-time response is linear in \( t \) and given by
\[
\langle \Psi_{\alpha}(t) | \mu_\alpha | \Psi_{\alpha}(t) \rangle \approx \frac{e^2 k}{m} N_e t.
\] (31)

D. Time-dependent density functional theory

The basic variables in Kohn-Sham density functional theory are the orbitals \( \phi_i(\vec{r}) \), which are varied to minimize an energy expression \( E_{KS} \) that contains the quantum kinetic operator and terms depending on the density \( n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2 \). The formal variation of the \( E_{KS} \) energy expression with respect to an orbital gives the Kohn-Sham operator \( H_{KS} \). In the time-dependent extension of DFT with the adiabatic approximation, the operator \( H_{KS} \) also used in the equation of motion for the orbitals. To linear order in the magnetic field strength \( B \), the time-dependent orbitals satisfy the equations
\[
\left[ H_{KS} + \mu B \vec{L} \cdot \vec{B} \right] \psi_i(t) = i \frac{\partial}{\partial t} \psi_i(t).
\] (32)

These equations are solved for \( \psi_i(t) \) with initial condition \( \psi_i(t = 0_+) = e^{i k \mu_\beta} \phi_i(\vec{r}) \), where \( \phi_i \) are the ground-state Kohn-Sham orbitals. The time-dependent response is calculated as
\[
S^{(\gamma)}_{\alpha\beta}(t) = \sum_i \langle \psi_i(t) | \mu_\alpha | \psi_i(t) \rangle.
\] (33)

For the calculations described below, we treat only the valence electrons dynamically and ignore any spin dependence. The effects of core electrons are treated by using Troullier-Martins pseudopotentials for the electron-ion interaction [24]. We use the usual LDA functional [25] for the exchange-correlation interaction as in previous work [26].
III. COMPUTATIONAL ASPECTS

The implementation of our real-time TDDFT is described in detail in Ref. [9]. An important difference from other TDDFT codes is the orbital representation in 3-dimensional Cartesian mesh. This has the computational benefit that the Kohn-Sham operator is given by a sparse matrix. The representation is also convenient for treating extended wave functions such as Rydberg states or continuum states. It has the disadvantage, however, that it does not permit all-electron calculations with practical mesh sizes. For checking our code, we found it helpful to calculate the observables with the Troullier-Martins pseudopotential replaced by an anisotropic harmonic oscillator potential. All the observables in this model have analytic expressions that can be compared with the calculated numerical quantities. See the Appendix for details.

In our implementation of the mesh representation, the momentum operator $p$ is computed by the 8-point difference function, which is consistent with our treatment of the kinetic operator $p^2/2m$ as a sum of 9-point difference functions along the three Cartesian axes. The main numerical parameters in the calculation are the mesh spacing $\Delta x$, the size of the spatial domain on which the orbital wave functions are defined, the time step $\Delta t$, and the total integration time $T$. We find that adequate precision for our purposes is obtained with parameter values $\Delta x = 0.5$ and $\Delta t = 0.03$ in atomic units. The spatial dimensions needed for the orbital wave functions depend on the desired accuracy in the continuum region. The continuum strength functions are smooth only if the spatial domain is large and absorbing boundary conditions are applied at the edges. Typically, we take a cubical box of $160^3$ mesh points for the calculations. For small molecules, a much smaller domain is adequate if the details of the response in the continuum are not needed.

Although the TDDFT is fundamentally nonperturbative, the quantities we calculate are in fact the perturbative limits with respect to the strengths of the applied magnetic and electric fields. We thus choose strengths that are small enough for the linear response formula to apply, but large enough to avoid numerical roundoff errors. For the perturbing electric field, we take $k = 0.001$. For the magnetic field, the calculations reported below were carried out with a magnetic field given by $\mu_B B = 0.0005$ au. The intensity of this magnetic field is 0.137 au. For comparison, a field strength of one Telsa has the value $5.81 \times 10^{-4}$ in atomic units.
The integration time $T$ required to calculate the response depends on the desired energy resolution. We multiply the integrands in the Fourier transforms Eq. (20) and Eq. (22) by the filter function $1 - 3(t/T)^2 + 2(t/T)^3$ to smooth out spurious oscillations from the upper time cutoff. The resulting peaks associated with sharp states have a width $\Gamma$ (full width at half maximum) given approximately by $\Gamma \approx 6/T$. Most of our results were calculated by integrating $N_t = 60000$ time steps, giving $\Gamma \approx 6/(N_t \Delta t) \sim 0.0033$ au = 0.1 eV.

IV. APPLICATION TO C$_{60}$

The C$_{60}$ molecule offers a good test of the methodology to demonstrate the feasibility of using the real-time method as applied to fairly large molecules. Due to the high symmetry of C$_{60}$, all optically allowed transitions are three-fold degenerate and there will be both $A$ and $B$ terms in the MCD spectrum. There are 5-6 excitations in the calculated spectrum up to 6 eV, all of which are $\pi - \pi^*$ character. It has been found that the experimental oscillator strength [27, 28] accords well with the theory [26] based on the ab initio adiabatic local density approximation.

Our calculation here is very similar to that carried out in Ref. [26] for the oscillator strength function. The integration time in the present calculation is somewhat longer, 60,000 time steps with $\Delta t = 0.03$ au. Before examining the MCD response, we recall the results for the ordinary dipole response, as calculated in the real-time method. Fig. 1 shows the $S_{zz}(t)$ real-time response over the interval $[0, T] = [0, 25]$ fs with the left-hand panel showing an expanded view of the first 0.275 fs time interval. The short-time behavior expected from Eq. (31) is shown by the straight dotted line in the left-hand panel. One may see that the initial response does indeed follow Eq. (31) very well. After the initial rise in the first 0.1 fs the dipole moment oscillates with a period of order of one fs corresponding to the strong transitions in the energy interval 7-15 eV. Note that the oscillation is essentially undamped. This is a consequence of the sharpness of the bound excitations that would produce a $\delta$-function response if the Fourier transform could be done exactly. The numerical Fourier transform was carried out to final time $t = 1800$ au = 43.5 fs with the results for the low-frequency part of $R_D(E)$ shown in the left-hand panel of Fig. 2. There are four transitions in the spectral region 0-6 eV, at excitation energies of 3.5, 4.3, 5.3 and 5.9 eV. The numerical FWHM widths are about 0.1 eV, as expected from the integration time. The important information besides
FIG. 1: Real-time dipole response \( S_{zz}(t) = \langle \Psi_{kz}(t) | \mu_z | \Psi_{kz}(t) \rangle \) for \( C_{60} \). The left-hand panel shows the time interval \( t = 0 - 0.275 \) fs with a linear time scale. The sloping line shows the expected short-time behavior according to Eq. \( (31) \). The right-hand panel shows the time interval \( t = 0.25 - 25.0 \) fs on a logarithmic time scale.

FIG. 2: Dipole response for \( C_{60} \). The differential oscillator strength \( df/dE \) (Eq. \( (6) \)) up to 6 eV is shown in the left-hand panel. The right-hand panel shows the integrated oscillator strength function \( f_E \), Eq. \( (29) \).

the transition energy is total strength in the individual peaks. This can be extracted from the graph of the integrated strength \( f_E \) defined in Eq. \( (29) \). The jumps at low energies give the \( f \) strengths of the discrete transitions. The total integrated strength is \( f = 233 \), rather close to the sum rule number \( f = 240 \) for the \( N_e = 240 \) valence electrons treated dynamically in the TDDFT. We note that the sum rule is not expected to be satisfied exactly for our energy functional, because of nonlocality in the Troullier-Martins pseudopotential.
FIG. 3: MCD real-time response $S_{xy}^{(z)}$ in C$_{60}$. The solid line in left-hand panel shows the evolution for short times, $0 < t < 0.3$ fs. The dotted curve is the expected dependence from Eq. (28). The long-dashed curve shows the response in the time range $0 < t < 0.07$ fs with the nonlocality in the pseudopotential turned off. The right-hand panel shows the response in the longer time interval $0.25 < t < 40$ fs on a logarithmic time scale and a magnified ordinate scale.

We now take up the MCD response. The left-hand panel of Fig. 3 shows the calculated MCD real-time response $S_{xy}^{(z)}(t)$ over the time interval $0 < t < 0.3$ fs. The dashed curve in the left-hand panel shows the predicted short-time dependence according to Eq. (28). The computed time dependence starts out quadratic as expected, but the coefficient of $t^2$ is lower by 40% than expected from Eq. (28). To confirm that the nonlocality of the pseudopotential is responsible for the disagreement, we have recomputed the response for short times with nonlocality of the pseudopotentials turned off, shown as the long-dashed line in the Figure. This agrees closely with the expected short-time behavior. We do not have any explanation why the sum rule violation is much stronger for the MCD strength than for the ordinary dipole strength.

The MCD response going to long times is shown on the right-hand panel of Fig. 3. It is interesting to note that the amplitude of oscillation increases with time. This behavior is in contrast to the ordinary dipole response, which has a maximum excursion in the first oscillation. The reason for the increase in amplitude is the presence of the $A$ terms which give a real-time response that cancels at short times and only becomes visible at later times. Taking the Fourier cosine transform of the real-time response using Eq. (20), we find the MCD spectrum shown in Fig. 4 left-hand panel. The $A$-type character of the
\( \pi - \pi^* \) transitions is clearly seen in the shape of curves, each with a strong alternation of sign over the width of the peaks in the dipole response function. (Again, there is no physical significance to the calculated widths since they depend on the integration limit in the Fourier transform.) It is interesting to see that the sign of \( A \) coefficients can vary from state to state. The excitation at 5.9 eV has the normal sign, namely negative on the low-frequency side, but the three lower excitations have the opposite sign. The four transitions in the figure also have a significant \( B \)-type MCD response, visible by unequal positive- and negative-going peaks on the two sides of the transition. The \( B \)-type response may be seen more clearly in the graph of the integrated MCD response, \( \int E \, dE' R_{\text{MCD}}(E') \), shown on the right-hand panel of Fig. 4. The \( B_n \) coefficients can be read off from the step increases going across each transition, cf. Eq. (9). The values are reported in Table I, divided by the theoretical dipoles strengths \( D_n \) (Eq. (12)). This is to facilitate comparison to the experimental values [29], which are given in this form. We see that the signs of \( B_n \) for the lowest two states agree. This is far from trivial. Also, the calculated magnitude of the lower one is within a factor of 2 of experiment. This is poorer agreement than is typical for the calculation of oscillator strength \( f_n \) in TDDFT, but perhaps this should not be unexpected due to the difficulties uncovered by the unexpected short-time behavior. Also, we know that there is considerable screening of the valence electron transition moments, amplifying the relative errors of the screened observables. The \( B_n \) of the second state has a much larger discrepancy. Until that is understood, one cannot use the TDDFT as a predictive tool for large molecules.

For a overall view of the MCD response, the right-hand panel of Fig. 4 shows the integrated MCD response up to 50 eV. The integrated response is predominantly negative, as to be expected with the negative-going initial evolution. One sees that the total goes to zero at the upper energy, showing that the \( I_0 \) sum rule (Eq. (26)) is nearly satisfied. Finally, the \( E^2 \) sum rule, Eq. (27), has a value \( J_2 = 258 \), almost a factor of two smaller than the nominal value of \( 2N_e = 480 \). We have already seen this effect of the nonlocality in the short-time response.

We next turn the \( A \)-type response, arising from the energy splitting between members of \( ^1T_{1u} \) multiplets as in the Zeeman splitting. A convenient way to express the splitting is as the effective \( g \)-factor for the transition [1][Eq. (52)],

\[
g = \frac{\Delta E}{\mu_B B}.
\]  

(34)
FIG. 4: MCD response $R_{\text{MCD}}(E)$ in $C_{60}$. Left-hand panel shows the strength function Eq. (4). The corresponding integrated strength function is shown in the right-hand panel.

TABLE I: MCD response of the lowest four $^1T_{1u}$ states in $C_{60}$. The experimental data is from Ref. [29]. Our calculations are given in the columns labelled TDDFT. The effective orbital $g$-factor is defined in Eq. (34).

| Energy (eV) | $B_n/D_n$ | $g$          |
|-------------|-----------|--------------|
|             | Exp. TDDFT | Exp. TDDFT   | Exp. TDDFT | Ref. [30] |
| 3.8         | 3.5       | 100          | 64         | $-0.3 \pm 0.05$ | $-0.97$ | $-1.0$ |
| 4.9         | 4.3       | -700         | -146       | $-0.55 \pm 0.15$ | $-0.58$ | $-0.75$ |
| 6.0         | 5.3       | 66           |            | $-0.20$ | $+0.12$ |
| 5.9         |           | -120         |            |            |            | $+0.35$ |

This is related to $A_n$ by

$$g = \frac{A_n}{2D_n}$$

(35)

We extract the $A_n$ coefficients by Eq. (8) from $R_{\text{MCD}}(E)$. We may also extract the energy shift $\Delta E$ from the zero-field value using the formula

$$\Delta E = -\mu_B B \int_{E_{n0}}^{E_{n0+\epsilon}} dE R_{\text{MCD}}(E) - \int_{E_{n0}}^{E_{n0+\epsilon}} dE \frac{R_{\text{MCD}}(E)}{4R_D(E_{n0})}$$

(36)

The extracted $g$-factors are shown in Table I along with the measured values [29] and results of a model calculation [30]. As with the $B_n$ values, we see agreement on sign for the two measured transitions. However, only the upper transition has a magnitude consistent with experiment.
V. CONCLUDING REMARKS

We have shown that from a computational point of view, the real-time method is a practical approach to calculate the MCD response in TDDFT. In particular, the entire response in the energy region of valence-electron excitations is obtained from a single calculation. This allows one to use the sum rules, at least as a theoretical tool, to understand the limitations with respect to the omission of core electrons from the dynamics. It would be exceedingly challenging to ensure that the sum rules Eqs. (26) and (27) are obeyed in formalisms that require the explicit construction of the excited state spectrum.

The violation of the sum rule Eq. (27) in the valence particle space raises an issue that needs to be addressed in future work. In Ref. 31, it was found that the violation of the dipole response in TDDFT is largely justified. The dynamic contribution of the core electrons shifts oscillator strength down into the spectral region of valence electrons, and this accounts physically for the increase of the sum rule, calculated only with valence electrons employing the nonlocal pseudopotential in the space of valence electron excitations. Whether there is a related mechanism to the decrease in the $I_2$ sum rule remains to be seen. Also, the pseudopotential should in principle be corrected for the gauge field associated with the magnetism, but that was not done here. It should be mentioned that these questions will also arise on calculations using the Projected Augmented Wave (PAW) method 32, since this also makes the Kohn-Sham operator nonlocal.

It was also a surprise to us to find that the MCD response may have an abnormal sign. This goes against the picture of an electron being excited to a higher band of orbitals and there undergoing circular motion in the sense given by the external magnetic field. It might be that strong screening destroys the simple connection to the expected classical oscillation picture. This raises another question for future work, to investigate in a general way the effects of screening on the MCD.

Finally, we have not discussed here the sensitivity to specific density functionals. Although not reported, we have also carried out the $C_{60}$ calculations with the LB94 functional 33. This gave very similar results except for Rydberg transitions, which are considerably shifted in energy, depending on the functional. Since the observables in MCD depend on currents, it might also be interesting to investigate the generalized TDDFT including current-current interactions.
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Appendix

In this Appendix we apply the real-time theory to a simple Hamiltonian, a spinless electron in an anisotropic harmonic oscillator potential. The model is completely solvable making it useful in checking the coding and formulas for the TDDFT in a magnetic field.

The Hamiltonian $H_0$ in Eq. (1) is taken as

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} \sum_\alpha m \omega_\alpha^2 r_\alpha^2$$

(37)

We label the eigenstates of $H_0$ by the number of excitation quanta along each coordinate axis, $|n_xn_yn_z\rangle$, and we set $m = e = \hbar = 1$ in the equations below. We take the oscillator frequencies $\omega_\alpha$ to be nondegenerate, so the MCD response will only have $B$-type contributions. We first need the eigenstates in the presence of the magnetic field, expanded to first order in the field strength. Taking the magnetic field in the $z$-direction, the relevant perturbed orbitals are

$$|000, B_z\rangle = |000\rangle - is_0|110\rangle$$

$$|100, B_z\rangle = |100\rangle - is_1|010\rangle$$

$$|010, B_z\rangle = |010\rangle - is_1|100\rangle$$

where

$$s_{0,1} = \frac{\mu_B B_z}{2} \frac{\omega_y \pm \omega_z}{(\omega_y \pm \omega_z)(\omega_x\omega_y)^{1/2}}.$$

(39)

The perturbed energies of the orbitals are not needed because that perturbation is second order in $B_z$.

To get the real-time response $S_{xy}^{(z)}$, we multiply the ground state wave function by the field $e^{ik\mu_y}$ and expand over the eigenstates, to first order in $k$. The required matrix elements of the dipole operator between ground and excited states are

$$\langle 100, B_z | \mu_x | 000, B_z \rangle = (2\omega_x)^{-1/2}.$$

(40)
\begin{align*}
\langle 010, B_z | \mu_y | 000, B_z \rangle &= (2\omega_y)^{-1/2} \\
\langle 010, B_z | \mu_x | 000, B_z \rangle &= -i\mu_B B_z (2\omega_y)^{1/2}/(\omega_x - \omega_y) \\
\langle 100, B_z | \mu_y | 000, B_z \rangle &= -i\mu_B B_z (2\omega_x)^{1/2}/(\omega_x - \omega_y)
\end{align*}

The initial perturbed wave function is

\[ |\Psi_{k_y}(t = 0)\rangle = |000, B_z\rangle + \frac{k}{(2\omega_y)^{1/2}} |010, B_z\rangle + \mu_B B_z k \frac{(2\omega_x)^{1/2}}{(\omega_x - \omega_y)} |100, B_z\rangle. \tag{41} \]

The time dependence is put in by multiplying the excited states by \( e^{-i\omega_\alpha t} \). The expectation value of \( \mu_x \) may then be evaluated as a function of time. The result after some simplification is

\[ S^{(z)}_{xy} = \frac{2k\mu_B B_z}{\omega_x - \omega_y} (\cos \omega_x t - \cos \omega_y t). \tag{42} \]

The short-time response given by Eq. (27) may be verified by making a power series expansion of the cosine functions in Eq. (42). Finally, the evaluation of \( R_{\text{MCD}} \) by Eq. (20) may be verified by carrying out the cosine Fourier transform,

\[ \frac{2}{\pi} \int_0^\infty dt \cos \omega t \cos \omega_0 t = \delta(\omega - \omega_0). \]

Putting in all three magnetic moment directions, the result is

\[ R_{\text{MCD}} = -\frac{1}{3} \frac{1}{\mu_B B} \sum_{\beta \neq \alpha} \delta(E - \omega_\alpha) \frac{2}{\omega_\alpha^2 - \omega_\beta^2}. \tag{43} \]

It may be easily verified that \( R_{\text{MCD}} \) satisfies the two sum rules, Eq. (25) and (26).

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