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ABSTRACT
We present a general variational approach for computing the laser-induced rovibrational dynamics of molecules, taking into account the hyperfine effects of the nuclear quadrupole coupling. The method combines the general variational approach TROVE (Theoretical Ro-Vibrational Energies), which provides accurate rovibrational hyperfine energies and wavefunctions for arbitrary molecules, with the variational method RichMol, designed for generalized simulations of the rovibrational dynamics in the presence of external electric fields. We investigate the effect of the nuclear quadrupole coupling on the short-pulse laser alignment of a prototypical molecule CFClBrI, which contains nuclei with large quadrupole constants. The influence of the nuclear quadrupole interactions on the postpulse molecular dynamics is negligible at early times, for the first several revivals; however, at longer time scales, the effect is entirely detrimental and strongly depends on the laser intensity. This effect can be explained by dephasing in the laser-excited rotational wavepacket due to irregular spacings between the hyperfine-split nuclear spin states across different rotational hyperfine bands.

Laser-controlled rovibrational molecular dynamics is a subject of active research in physics and chemistry.1–4 In particular, the control of molecular spatial alignment and orientation5–7 is highly leveraged in many ultrafast imaging experiments8–14 and stereochemistry studies15–17 to increase the experimental resolution. The mechanism of the alignment and orientation is tied to the driven rotational dynamics of molecules in the ground vibrational state and described by two-photon18,19 or three-photon20,21 Raman excitation processes. The adiabatic alignment is induced by slowly increasing the laser electric field, which creates directional potential trapping molecules in pendular states. Adiabatic alignment combined with a DC electric field produces the mixed-field orientation of molecules.22,23 In the impulsive alignment regime using short laser pulses, the created rotational wavepacket evolves with repeated alignment/orientation and antialignment revivals. In all of these schemes, the temporal evolution of the rotational wavepacket and the resulting revival structure is characteristic of the rotational-energy-level structure of the molecule.24–25 Typically, this temporal wavepacket evolution is accurately predicted using the rigid-rotor or semirigid rotor Hamiltonian models.26–28 Many heavy atoms, such as bromine, iodine, or platinum, have large nuclear quadrupoles. In molecules, these create large hyperfine splittings, comparable to or even larger than the rotational-energy spacings. These strong hyperfine interactions arise from the coupling between the quadrupole moments of nuclei and the electric field gradients produced by the distribution of nuclei and electrons through the molecule. In such heavy-atom-containing molecules, the presence of the manifold of hyperfine-split nuclear-spin states makes the temporal evolution of the laser-excited rotational wavepacket, and thus the alignment revival structure, more complicated.29 Therefore, a detailed understanding of the effect of these nuclear-quadrupole interactions is an important ingredient for the control over the alignment of heavy-atom-containing molecules, with corresponding implications for molecular-frame imaging experiments. Heavy atoms are commonly utilized as strong scattering and absorption centers in x-ray imaging experiments.30,31 They are also exploited as good leaving
groups in Coulomb-explosion velocity-map imaging of molecular dynamics.\textsuperscript{32,33}

Here, we present a general variational approach for computing the field-driven rovibrational dynamics of molecules including nuclear-quadrupole interactions. The present approach extends our previously reported variational method for computing the nuclear-quadrupole hyperfine spectra of small molecules.\textsuperscript{7} We developed a generalized methodology for computing the matrix representations of various electric-multipole-moment tensor operators in the basis of hyperfine wavefunctions. These tensor operators are used as building blocks of the molecule-field interaction potential in simulations of the field-driven rovibrational dynamics, as implemented in the computational approach RichMol.\textsuperscript{1} To our knowledge, this is the first attempt to generalize simulations of this kind. We demonstrate the effect by calculating the one-dimensional alignment dynamics of the asymmetric CF\textsubscript{3}Cl.\textsuperscript{151}

In brief, in RichMol, the time-dependent wavepacket $\Psi(t)$ is built from a superposition of the field-free rovibrational wavefunctions $|J, m_J, l\rangle$,\textsuperscript{34}

$$\Psi(t) = \sum_{J, m_J, l} c_{J, m_J, l}(t) |J, m_J, l\rangle,$$  \hspace{1cm} (1)

where $J$ and $m_J$ denote the quantum numbers of the total rotational angular momentum operator $\hat{J}$ and its projection onto the laboratory-fixed $Z$ axis, respectively. $l$ represents a set of additional rotational and vibrational quantum numbers. The time-dependent coefficients $c_{J, m_J, l}(t)$ are determined by a numerical solution of the time-dependent Schrödinger equation using the time-evolution operator method. The total Hamiltonian consists of the sum of the molecular rovibrational Hamiltonian $H_{\text{rv}}$, with the eigenfunctions $|J, m_J, l\rangle$, and the molecule-field interaction potential $V(t)$, expanded in terms of molecular electric multipole moment operators,

$$H(t) = H_{\text{rv}} - \mu_A E_A(t) - \frac{1}{2} \alpha_{AB} E_{AB}(t) + \cdots.$$  \hspace{1cm} (2)

$A$ and $B$ are Cartesian indices denoting the $X$, $Y$, and $Z$ axes in the laboratory frame, and the summation over all Cartesian indices is implicitly assumed. $E_{AB}(t)$ is the $A$ Cartesian component of the electric field vector, and $\mu_A$ and $\alpha_{AB}$ are the electronic contributions to the molecular-frame electric-dipole-moment vector and polarizability tensor, respectively. The interaction terms of the higher expansion order, such as the first and second hyperpolarizability tensors, can also, in principle, be included in the sum in (2).\textsuperscript{35}

The time-evolution operator for the time step $\Delta t = t - t'$ is computed using the split-operator method as

$$U(t, t') = e^{-i \int_{t'}^{t} H_{\text{rv}}(\tau) d\tau} \left( e^{i \frac{\mu_A E_A(t')}{\hbar}} e^{i \frac{\alpha_{AB} E_{AB}(t')}{\hbar}} e^{i \frac{\alpha_{BC} E_{BC}(t')}{\hbar}} \cdots \right) e^{-i \int_{t'}^{t} H_{\text{rv}}}.$$  \hspace{1cm} (3)

$H_{\text{rv}}$ is diagonal in the basis of its eigenfunctions $|J, m_J, l\rangle$, and the diagonal elements are the molecular rovibrational energies. The exponents of the Cartesian tensor operators $\mu_A, \alpha_{AB}, \ldots$ are evaluated using an iterative approximation based on the Krylov-subspace methods. The computational performance of the iterative methods depends crucially on how efficient the matrix-vector products can be computed between the operator exponential and the subspace vectors. In the following, we will use $T_{\text{A}}^{(1)}$ to denote any index-symmetric Cartesian tensor operator of rank $\Omega$, with $A$ being multi-index labeling Cartesian components in the upper simplex of the tensor in the laboratory frame. For example, for the dipole moment, $\Omega = 1$ and $A = X, Y, \text{or} Z$, and for the polarizability tensor, $\Omega = 2$ and $A = XX, XY, XZ, YY, YZ, \text{or} ZZ$.

The computations of the matrix-vector products can be significantly sped up by expressing the matrix representation of Cartesian tensor operators $T_{\text{A}}^{(1)}$ in a contracted tensor form,

$$\langle J', m_J', l' | T_{\text{A}}^{(1)} | J, m_J, l \rangle = \sum_{\omega=0}^{\Omega} \mathcal{M}_{\text{A}, \omega}^{(J', m_J', l')} \mathcal{K}_{\omega}^{(J', l', J)}.$$  \hspace{1cm} (4)

The sum runs over all irreducible representations $\omega$ of the tensor, and the matrices $\mathcal{M}_{\text{A}, \omega}^{(J', m_J', l')}$ and $\mathcal{K}_{\omega}^{(J', l', J)}$ decouple the laboratory-frame projections $A$ and quantum numbers $m_J$ and $m_J'$ from the molecular-frame rovibrational quantum numbers $l$ and $l'$.

The explicit expressions for the $\mathcal{M}_{\text{A}, \omega}$ and $\mathcal{K}_{\omega}$ matrices depend on the form of the field-free wavefunctions $|J, m_J, l\rangle$. We use the general-molecule variational approach TROVE (Theoretical Ro-Vibrational Energies)\textsuperscript{36} to compute the field-free energies and wavefunctions $|J, m_J, l\rangle$, which are represented by linear combinations of products of vibrational wavefunctions $|\nu\rangle$ and symmetric-top rotational functions $|J, m_J, k\rangle$,

$$|J, m_J, l\rangle = \sum_{\nu, k} c_{\nu, k}^{J, m_J, l} |\nu\rangle |J, m_J, k\rangle.$$  \hspace{1cm} (5)

$\nu$ denotes the composite vibrational quantum number, and $k$ denotes the quantum number of the molecular-frame $z$-projection of the rotational angular momentum operator. Using the wavefunctions from (5), the expressions for $\mathcal{M}_{\text{A}, \omega}$ and $\mathcal{K}_{\omega}$ can be derived as

$$\mathcal{M}_{\text{A}, \omega}^{(J', m_J', l')} = (-1)^{\Omega} \sqrt{(2 \Omega + 1)(2J + 1)} \sum_{\alpha=\omega}^{\Omega} \left[ U_{\Omega,\alpha}^{(1)} \right]_{\text{A}, \omega} \left( \begin{array}{ccc} J & \omega & J' \\ m_J & m_J' & \end{array} \right)$$  \hspace{1cm} (6)

$$\mathcal{K}_{\omega}^{(J', l', J)} = \sum_{k, \omega'} \left[ U_{\omega,\omega'}^{(1)} \right]_{\text{A}, \omega} \sum_{\rho} \left( \begin{array}{cc} l' & \omega \\ k & \omega' \end{array} \right) c_{\rho}^{J, l', J} (-1)^{-\Gamma} \sum_{\sigma, \sigma'} \left( \begin{array}{cc} \sigma & \sigma' \\ k & \sigma' \end{array} \right) U_{\sigma,\sigma'}^{(1)} |\nu\rangle |J, m_J, l\rangle.$$  \hspace{1cm} (7)

$T_{\text{A}}^{(1)}$ denotes the Cartesian tensor operator in the molecular frame, with $a$ being a Cartesian multi-index (similar to $A$), and the matrix $U_{\Omega,\alpha}^{(1)}$ defines the transformation of the tensor from Cartesian to spherical-tensor form.\textsuperscript{35}

This approach is general and can be interfaced with any rovibrational code that provides the tensor-matrix elements in the form of (4). The approach also permits the use of more complex field-free wavefunctions than those defined in (5). As multipole-moment operators commute with the nuclear-spin angular momenta, the operators’ matrix elements in the basis of hyperfine states can also be cast in the form of (4). In the following, we derive the explicit expressions for the $\mathcal{M}_{\text{A}, \omega}$ and $\mathcal{K}_{\omega}$ matrix elements in the basis of the nuclear-spin hyperfine-structure wavefunctions.

The general variational implementation of the nuclear-spin hyperfine effects at the level of the nuclear-quadrupole...
interaction was recently implemented\textsuperscript{14} and used for the generation of a quadrupole-resolved line list of the ammonia molecule.\textsuperscript{40} The nuclear-quadrupole interaction in a molecule containing \( n = 1 \ldots N \) quadrupolar nuclei is described by the coupling of the electric field gradient (EFG) tensor at each \( n \)th nucleus \( V(n) \) with its quadrupole moment tensor \( Q(n) \). The total spin-rovibrational Hamiltonian takes the form

\[
H_{\text{lev}} = H_R + \sum_n V(n) \cdot Q(n).
\]

The overall rotational, \( J \), the nuclear spin, \( I_n \), and total, \( F \), angular momentum operators for \( n = 1 \ldots N \) quadrupolar nuclei are coupled as \( I_{1,2} = I_1 + I_2, I_{1,3} = I_1 + I_3, \ldots, I_{1,N-1} = I_{1,N-2} + I_{N-1}, I \equiv I_{1,N} = I_{1,N-1} + I_N, \) and \( F = J + I \). The nuclear-spin functions \( |l, m_l, Z \rangle \) depend on the quantum numbers \( l \) and \( m_l \) of the collective nuclear spin angular momentum operator \( I \) and its projection onto the laboratory \( Z \) axis, respectively. The set of auxiliary spin quantum numbers \( \mathcal{I} = \{I_1, I_2, \ldots, I_{N-1} \} \) of the intermediate spin angular momentum operators provide a unique assignment of each nuclear-spin state. The total spin-rovibrational wavefunctions \( |F, m_F, u \rangle \) are built as symmetry-adapted linear combinations of the products of the rovibrational wavefunctions \( |l, m_l, l \rangle \) in (5) and the nuclear-spin functions \( |l, m_l, Z \rangle \).

\[
|F, m_F, u \rangle = \sum_{l,F,l,l} c_{l,l,F,l}^{(F,u)} \sum_{m_l} (-1)^{F+m_l} \sqrt{2F+1} \begin{pmatrix} I & m_l & m_l \end{pmatrix} |l, m_l, Z \rangle |l, m_l, l \rangle.
\]

(9)

\( c_{l,F,l,l}^{(F,u)} \) are the eigenvector coefficients of the spin-rovibrational Hamiltonian (8), \( F \) and \( m_F \) are the quantum numbers of \( F \) and its projection onto the laboratory-fixed \( Z \) axis, and \( u \) denotes the hyperfine-state running index.

The explicit expressions for the matrix elements of the spin-rovibrational Hamiltonian (8) for an arbitrary number of quadrupolar nuclei and details of the variational solution can be found in Ref. 34. Here, we derived explicit expressions for the matrix elements of the general electric multipole Cartesians tensor element \( (F', m_F', u'\mathcal{I}^{(0)}), (F, m_F, u) \rangle \), which, in the contracted-tensor form of (4), are

\[
\mathcal{M}_{\mu,\sigma}^{(F', m_F', F, m_F)} = \sum_{\omega} (U^{(0)} \sigma)^{-1} \sum_{\alpha=\omega} \alpha \begin{pmatrix} F' & \omega & F \\ \mu & \sigma & m_F \end{pmatrix}.
\]

(10)

and

\[
\mathcal{K}_{\mu,\sigma}^{(F', m_F', F, m_F)} = \sum_{\omega} \sum_{\alpha,\beta} \begin{pmatrix} c_{F', \mu}^{(F,u)} c_{\alpha,\beta}^{(F,u)} \end{pmatrix} \begin{pmatrix} c_{l,l,F,l}^{(F,u)} \end{pmatrix} (-1)^{\beta} \begin{pmatrix} (2F' + 1) & (2F + 1) \\ (2F' + 1) & (2F + 1) \end{pmatrix} \begin{pmatrix} F' & \omega & F \\ \mu & \sigma & m_F \end{pmatrix}.
\]

(11)

\( \mathcal{K}_{\mu,\sigma}^{(F', m_F', F, m_F)} \) defined in (7), contains the rovibrational matrix elements of \( I_A^{(3)} \) in the basis \( |l, m_l, l \rangle \). Using the expressions (10) and (11) in (4), RichMoL could directly be employed to simulate the coupled nuclear-spin-rovibrational molecular dynamics in external fields. In (3), the diagonal representation of \( H_{\text{lev}} \) in the rovibrational energies was replaced by the diagonal representation of \( H_{\text{lev}} \) in the hyperfine energies (8).

This new approach was used to investigate the effect of nuclear-quadrupole coupling (QC) on the impulsive alignment of bromochlorofluorodiodomethane CF\textsuperscript{35}Cl\textsuperscript{37}Br\textsuperscript{127}. This molecule has a quasi-rigid structure and contains three different heavy nuclei with large quadrupole coupling constants and with correspondingly nontrivial laser-induced rotational and nuclear spin spectra and dynamics. A short nonresonant laser pulse is linearly polarized along the laboratory \( Z \) axis. Its intensity is given by the Gaussian function \( I(t) = I_0 \exp(-4\ln 2t^2/\sigma^2) \) with \( \sigma = 1 \) ps and \( I_0 = 6 \times 10^{11} \) W/cm\(^2\) or \( 1 \times 10^{12} \) W/cm\(^2\). The excitation by a nonresonant laser field is described by the electric polarizability term in the interaction potential (2). The explicit expressions for the elements of the matrix \( \mathcal{K}^{(2)} \) for the polarizability are listed in Table I of Ref. 35. The degree of molecular alignment is characterized by the expectation value \( \langle \cos^2 \theta \rangle = \langle \Psi(\theta) | \cos^2 \theta | \Psi(\theta) \rangle \), with the angle \( \theta \) between the molecular-frame \( x \) and the laboratory-frame \( Z \) axes. The matrix elements of the cos\(^2 \) \( \theta \) operator can be easily computed using the general expressions (10), (11), and (7) by noting the relationship cos\(^2 \) \( \theta \) = \( 2d_{00} + 1 \)/3, where \( d \) is the Wigner \( d \) matrix. The vibrational matrix elements of \( d_{00} \) in (7) are \( \langle l' | \tilde{d}_{00} | v \rangle = \delta_{l'v} \) and \( U_{0,\alpha}^{(0)} = \delta_{m\alpha} \delta_{00} \); here, the index \( a \) in (7) is redundant.

For simplicity, we neglected the vibrational motion of the molecule and approximated the full rovibrational wavefunctions in (5) by rigid-rotor solutions. The rigid-rotor approximation in simulations of the laser-induced alignment of quasirigid and even nonrigid molecules in ultracold molecular beams has been validated in numerous studies.\textsuperscript{3,4,8,41-44} The zero-point vibrational corrections to various electromagnetic tensors are known to be quite small, on the order of 1%–3%, even for nonrigid molecules such as \( \text{H}_2\text{O}_2 \),\textsuperscript{45} and have been neglected in this study. The equilibrium geometry and polarizability of CFCI\textsuperscript{21}Br\textsuperscript{46} were calculated using density functional theory (DFT) with the B3LYP functional and the def2-TZVP basis set\textsuperscript{47} in conjunction with the relativistic effective core potential de2-ECP on the iodine atom.\textsuperscript{48} The accuracy of hybrid functionals for the prediction of molecular polarizabilities was assessed on a dataset of 132 molecules, yielding a root-mean-square error of 3%–5% relative to coupled-cluster singles and doubles with a perturbative correction to triples [CCSD(T)].\textsuperscript{49} Calculations of the electric field gradient tensors, needed for the nuclear-quadrupole coupling Hamiltonian in (8), were carried out at the DFT/B3LYP level of theory using the all-electron scalar relativistic Douglas-Kroll-Hess Hamiltonian\textsuperscript{50} with the DKH-de2-TZVP basis set.\textsuperscript{51,52} Systematic studies of the accuracy of DFT functionals for predictions of the electric field gradient tensors of transition metal complexes provided a mean error estimate of about 0.071 a.u. for the B3LYP functional.\textsuperscript{53} All electronic structure calculations employed the quantum chemistry package ORCA.\textsuperscript{54,55} The quadrupole moments for the 33Cl,\textsuperscript{56} 79Br, and 127I nuclei are \( Q = -81.65 \) mb, 313 mb, and -696 mb, respectively.\textsuperscript{57} The calculations of the molecule-field dynamics in the basis of the nuclear-spin hyperfine states were performed in a three-step
procedure: First, we solved the field-free problem using the rigid-rotor Hamiltonian and obtained the rotational energies and the rotational matrix elements of the EFG and the polarizability tensors, as well as of the \( \cos^2 \theta \) operator, (6) and (7). Then, we used the rotational energies and the matrix elements of the EFG tensors together with the nuclear-quadrupole constants to build and diagonalize the nuclear-spin quadrupole-coupling Hamiltonian.\(^{34}\) (8). We obtained the spin-rotational eigenfunctions in (9) and transformed the rotational matrix elements of the polarizability tensor and \( \cos^2 \theta \) operator into the spin-rotational eigenbasis using (10) and (11). Finally, we used the spin-rotational energies and the matrix elements of the polarizability to build the molecule-field interaction Hamiltonian and solve the time-dependent problem. The wavepacket \( \Psi(t) \) in (1) was built from a linear combination of spin-rotational wavefunctions with time-dependent coefficients. The expectation value \( \langle \cos^2 \theta \rangle \) is calculated from the spin-rotational matrix elements of \( \cos^2 \theta \) computed at the previous step.

Here, we used a rotational basis that included all spin-rotational states of CFClBrI with \( F \leq 41/2 \), corresponding to \( J \leq 26 \). We assumed that CFClBrI is initially in the ground rotational state \( J = 0 \), which has 96 different nuclear-spin state components, including the \( m_J \) degeneracy. Therefore, we performed a series of simulations starting from the different nuclear-spin components and averaged the results assuming equal normalized populations of different spin components. For comparison, we also performed calculations neglecting the hyperfine effects, i.e., using rigid-rotor wavefunctions as the field-free basis. It should be noted that samples of heavy molecules populating a few of the lowest rotational states, with \( T_{rot} \approx 0.4 \) K, can be produced from cold molecular beams using the electrostatic deflector.

The temporal evolution of the alignment calculated for two different laser intensities is shown in Fig. 1. For both laser intensities, the alignment without nuclear-quadrupole interaction shows complex revival patterns originating from the dephasing and rephasing of the rotational wavepacket. Since CFClBrI is an asymmetric-top molecule (asymmetry parameter \( \kappa = -0.73 \)), the revival patterns lack the typical periodicity of the \( J \)-type or \( C \)-type revivals observed for near-symmetric-top molecules.\(^{40,60,61}\) Notably, the broader wavepacket, produced by the higher-intensity pulse, shows higher-frequency oscillations and generally reduced peak alignment. This is ascribed to mismatches of the phases of the populated rotational states after the laser pulse\(^{34,42}\) and successive dephasing due to the molecule’s asymmetry,\(^{42}\) preventing the simultaneous rephasing of more than a few rotational states with significant populations.

The nuclear-quadrupole interaction increases the complexity of the revival dynamics and depletion of the peak alignment compared to the rigid-rotor results. Nevertheless, during the first 300 ps after the laser pulse, the degree of alignment is almost identical to the rigid-rotor result. We also observed a dependence of the nuclear-quadrupole effect on the laser-field intensity. For the lower intensity, Fig. 1(a), the impact is seen about 200 ps earlier than for the higher intensity, Fig. 1(b).

The nonperiodic recurrences in the alignment dynamics of the asymmetric-top molecules originate from large asymmetry splittings of the rotational energy levels. The influence of the nuclear-quadrupole interaction can be understood in a similar manner, as the dephasing effect resulting from the incommensurate hyperfine splittings for different rotational states. The dephasing is stronger for the wavepacket dominated by the low-energy rotational states, where the hyperfine splittings are mostly irregular. For large \( J \), the hyperfine splittings become increasingly uniform\(^{42}\) and the contribution to the dephasing is minimized. This explains why the effect of the nuclear-quadrupole interaction is less striking for the higher-intensity laser field, which populates higher-energy rotational states. For both intensities, however, the small-\( J \) states have relatively large populations and the nuclear-quadrupole interaction has a strong influence on the field-free alignment.

In conclusion, we have presented the first general implementation of nuclear-quadrupole hyperfine effects in the rovibrational dynamics of molecules driven by external electric fields. Our approach combines TROVE, which provides hyperfine energies and wavefunctions for the arbitrary molecule, with RichMol, designed for generalized simulations of external-field effects. In principle, the presented approach can be applied to simulate the fully coupled spin-rovibrational dynamics of any molecule with no inherent limitations on the number of quadrupolar nuclei. The external field...
effects are not limited by the polarizability interaction: other multi- 

pole moment operators, including the permanent dipole moment or 

the first and second hyperpolarizabilities, can be considered without 
addition implementation efforts.

We studied the influence of the nuclear-quadrupole coupling on the laser impulsive alignment of a prototypical heavy-atom molecule CFCIBr. While the effect is small for the first few revivals, it turns out to be entirely detrimental for the revivals at later times. The laser field plays an important role, with lower intensities prompting a larger effect of the nuclear-quadrupole coupling. This can be explained by dephasing of the rotational wavepacket due to the incommensurate structure of the hyperfine-split levels for different rotational states. This effect is stronger for small-/rota-
tional states and practically disappears for states with high angular 
moments. Given that small-J states in the wavepacket will be the 
source of the largest dephasing effects, we expect that stronger laser 
intensities and higher initial rotational temperatures should further 
diminish the effect of the nuclear-quadrupole coupling. More rig-
orous studies of these effects for different alignment scenarios and 

molecular systems are ongoing. We envisage future applications of 

the presented approach to inform and interpret diverse laser-field 
experiments on molecules containing nuclei with large quadrupole 

constants.

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