Parity Nonconserving Nuclear Spin Coupling in Molecules

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The weak interaction does not conserve parity, which is apparent in many nuclear and atomic phenomena. However, thus far, parity nonconservation has not been observed in molecules. Here we consider nuclear-spin-dependent parity nonconserving contributions to the molecular Hamiltonian. These contributions give rise to a parity nonconserving indirect nuclear spin-spin coupling which can be distinguished from parity conserving interactions in molecules of appropriate symmetry, including diatomic molecules. We estimate the magnitude of the coupling, taking into account relativistic corrections. Finally, we propose and simulate an experiment to detect the parity nonconserving coupling using liquid-state zero-field nuclear magnetic resonance of electrically oriented molecules and show that $^1$H$^{19}$F should give signals within the detection limits of current atomic vapor-cell magnetometers.

INTRODUCTION

Parity nonconservation (PNC) in the weak interaction was first theorized [1] in 1956, followed by the first experimental observation in $\beta$-decay of $^{60}$Co nuclei in 1957 [2]. In the decades since, a variety of parity nonconserving effects have been observed in atoms [3]. PNC should also be present in the molecular Hamiltonian, although its effects have not yet been observed. Molecules afford some interesting possibilities to observe PNC effects including proposals to observed energy shifts between enantiomers of chiral molecules [4,5], time-dependent optical activity in chiral molecules [6,7,8], and stark interference in diatomic molecules [9,10]. Molecules may also provide opportunities to study finer aspects of PNC. In particular, diatomic molecules are of interest because of the presence of closely-lying levels of opposite parity which are not a general feature of atoms other than hydrogen [11,12].

In this Letter, we propose to observe nuclear-spin dependent PNC via the indirect nuclear spin-spin coupling in molecules. It has been known for some time that PNC effects should cause frequency shifts between the nuclear magnetic resonance (NMR) spectra of enantiomers of chiral molecules [16,23]. Here we consider a different effect which can be observed in non-chiral molecules, including diatomic molecules. The indirect nuclear spin-spin, also called $J$-coupling, is a commonly measured property in nuclear magnetic resonance (NMR) spectroscopy [24,25]. The Hamiltonian for two coupled nuclei is bilinear with respect to spin operators $\hat{I}$ and $\hat{S}$. The isotropic or scalar $J$-coupling, which transforms under rotations as a rank-0 spherical tensor, is most commonly observed in liquid-state NMR spectroscopy. The corresponding Hamiltonian is:

$$\hat{H}_0 = 2\pi J \hat{I} \cdot \hat{S}. \quad (1)$$

Higher-rank contributions to the $J$-coupling can be observed in oriented molecules, for example the rank-1 coupling:

$$\hat{H}_1 = 2\pi J^{(1)} \cdot \hat{I} \times \hat{S}, \quad (2)$$

where $J^{(1)}$ has three independent components and transforms under rotations as a vector. The effects of $\hat{H}_1$ have not yet been observed since it averages to zero in isotropically rotating molecules and is suppressed in a magnetic field if spins $I$ and $S$ have different Larmor frequencies. It could, in principle, be observed in solids, but solid-state NMR typically suffers from low resolution. Zero-field nuclear magnetic resonance of electrically-oriented molecules can reveal signals from $\hat{H}_1$, as was proposed for absolute determination of molecular chirality [27]. We propose to observe the contribution of the nuclear-spin-dependent parity nonconserving weak interaction to $\hat{H}_1$ [28].

For uniaxially oriented molecules, a residual component of $J^{(1)}$ along the orientation axis survives the fast orientational averaging of a liquid-state small molecule. A parity nonconserving $J^{(1)}$ with a nonzero projection along the molecular electric dipole can be found in molecules belonging to several symmetry point groups (Supplemental Material) including diatomics ($C_{\infty v}$). Diatomics also have the advantage of no parity conserving contribution to $J^{(1)}$ along the dipole. We now estimate the magnitude of $J_{PNC}$ in the diatomics $^{205}$TI$^{19}$F...
and $^{1}$H$^{19}$F. $J_{PNC}^{(1)}$ arises from the nuclear-spin-dependent parity-odd weak interaction. For a first-order approximation, we only include terms that are linear in the nuclear spin operator $I_K$ (For the sake of notation we will use $I_k$ for a generic nuclear spin operator, but will use $\hat{I}$ and $\hat{S}$ when explicitly considering a 2-spin Hamiltonian for calculation of observables in an NMR experiment). We also neglect terms that contain electron spin operators since, to a first-order approximation, they do not contribute to PNC in the diamagnetic molecules under consideration [15]. In the non-relativistic approximation the Hamiltonian for the $J^{(1)}$ parity nonconserving interaction has the form (using atomic units $\hbar = m_e = |e| = 1$):

$$\hat{H}_{PNC} = \frac{G\alpha}{2\sqrt{2}} \sum_{i,K} g_K \hat{I}_K [p_i, \delta(r_i - R_K)]_+ ,$$  \hspace{1cm} (3)

The second term in Equation 5 is bilinear in nuclear spin operators and contributes to the spin-spin coupling [28]. By bond length and are about 3 — 4 Bohr radii. Given the genic, the two K-shell electrons, whose wavefunctions are hydro-

The electronic matrix elements in (6) correspond to the total electronic densities on the respective nuclei:

$$\langle \Psi_e | \sum_i \delta(r_i - R_K) | \Psi_e \rangle = \rho_e(R_K) .$$  \hspace{1cm} (7)

Substituting into (6) we obtain:

$$J_{PNC}^{(1)} = \frac{G\alpha}{\sqrt{2}} \left( g_{SgL}\rho_e(R_l) + g_{gL}\rho_e(R_S) \right) \frac{R_l - R_S}{|R_l - R_S|^3} .$$  \hspace{1cm} (8)

The dominant contribution to the density (7) comes from the two K-shell electrons, whose wavefunctions are hydrogenic, $\psi_{1s} \approx 2\sqrt{Z/4\pi} e^{-Zr}$, therefore

$$\rho_e(R_K) \approx \frac{2}{\pi} Z_K^2 .$$  \hspace{1cm} (9)

The contribution of the 2s shell is approximately 8 times smaller and can be neglected in the estimates (for hydrogen the density at the origin scales as $1/r^3$). Typical internuclear distances $|R_l - R_S|$ are comparable to the bond length and are about 3 — 4 Bohr radii. Given the $Z^3$ scaling, the term in parentheses in Equation 8 including $Z$ from the heaviest atom will dominate. Assuming

where $G \approx 2.22 \times 10^{-14}$ is the Fermi constant, $\alpha \approx 1/137$ is the fine-structure constant, $g_K$ is dimensionless coupling constant of order unity [15], $p_i = -i\nabla_i$ and $r_i$ are momentum and coordinate of $i$-th electron, and $R_K$ is coordinate of the nucleus $K$. To account for a magnetic field, we substitute the canonical momentum $p_i \rightarrow p_i + \alpha A$, where $A$ is vector potential. In the case of spin-spin coupling, the magnetic field is produced by the magnetic moment of nucleus $L$: $\mu_L = g_L\mu_{nuc}I_L$. We can then take:

$$\hat{A}_L = g_L I_L \times (r - R_L) / |r - R_L|^3 .$$  \hspace{1cm} (4)

Substituting Equation 4 in Equation 3 we obtain:

$$|R_K - R_L| \approx 4$$ the magnitude of $J_{PNC}^{(1)}$ is estimated:

$$J_{PNC}^{(1)} \approx \frac{G\alpha}{\sqrt{2}} g_{SgL} \approx \frac{1}{8\pi} Z_I^3 ,$$  \hspace{1cm} (10)

where $Z_I$ is the charge of the heaviest nucleus in the molecule.

For heavier atoms, relativistic effects can become important. The relativistic enhancement factor is (Supplemental Material):

$$F_{rel} = \frac{2(1 + \gamma)(2ZR_{nuc})^{2\gamma - 2}}{\Gamma^2(2\gamma + 1)} , \hspace{1cm} \gamma = \sqrt{1 - (\alpha Z)^2} ,$$  \hspace{1cm} (11)

where $R_{nuc}$ is the distance between the nuclei and $\Gamma$ refers to a gamma function. Equation 10 becomes:

$$J_{PNC}^{(1)} \approx F_{rel} \frac{G\alpha}{\sqrt{2}} g_{SgL} \frac{1}{8\pi} Z_I^3 .$$  \hspace{1cm} (12)

We now make estimates of the magnitude $J_{PNC}^{(1)}$ for the molecules $^{205}$Tl$^{19}$F and $^{1}$H$^{19}$F. TlF is a popular candidate for molecular PNC searches because the heavy $^{205}$Tl atom ($Z=81$) is expected to give rise to strong PNC effects. From Equation 12 we obtain:
while this value is promising given the resolution of zero-field NMR, diatomic TIF does not exist in the liquid phase and zero-field NMR would be a significant experimental challenge. HF, however, is a liquid below 20°C and provides high-resolution NMR spectra [29]. The estimated PNC coupling for $^1$H$^{19}$F is:

$$J^{(1)}_{\text{PNC,TIF}} \approx 19 \times 10^{-3}\text{Hz.} \quad (13)$$

While this value is promising given the resolution of zero-field NMR, diatomic TIF does not exist in the liquid phase and zero-field NMR would be a significant experimental challenge. HF, however, is a liquid below 20°C and provides high-resolution NMR spectra [29]. The estimated PNC coupling for $^1$H$^{19}$F is:

$$J^{(1)}_{\text{PNC,HF}} \approx 19 \times 10^{-6}\text{Hz.} \quad (14)$$

$J^{(1)}_{\text{PNC}}$ is fixed with respect to the molecular orientation, but small molecules in the liquid state undergo fast molecular rotation. In NMR, we measure the averaged tensor $J^{(1)}_{\text{PNC}}$ which is nonzero only when the molecules are oriented. Applied electric fields up to 60 kV/cm have been used to orient molecules for high-resolution NMR [30]. The high dielectric constant ($\varepsilon_r = 86$) of HF will enhance the applied field and the electric dipole moment ($\mu = 1.86\text{D}$) is amenable to electric field orientation. An applied field of 60 kV/cm at temperature 300 K gives an orientational order parameter of 0.09 (Supplemental Material). We therefore use $J^{(1)}_{\text{PNC,HF}} = 1.7 \times 10^{-6}\text{ Hz}$ for the estimated projection of $J^{(1)}_{\text{PNC,HF}}$ along the z-axis. Zero-field NMR involves measuring the evolution of nuclear magnetism of coupled spins in the absence of external magnetic fields [31] (Figure 1h). Signals are typically detected by an atomic vapor cell magnetometer. When a diatomic molecule is oriented along the z-axis such that $J_{\text{PNC}}$ is nonzero, the nuclear spin Hamiltonian is:

$$\hat{H} = 2\pi J \hat{I} \cdot \hat{S} + 2\pi \frac{i J_{\text{PNC}}}{2} (\hat{I}^+ \hat{S}^- - \hat{I}^- \hat{S}^+), \quad (15)$$

which is a result of Equation 2 when only the z-component of $J^{(1)}$ is nonzero. Rapid motion around the z-axis averages components of $J^{(1)}\parallel$ orthogonal to the z-axis to zero. $J$ is the scalar component of the $J$-coupling which is not affected by molecular rotation. Assuming $|J_{\text{PNC}}| \ll |J|$ and $I = S = 1/2$, the eigenstates are the singlet and three degenerate triplet states, with an energy separation equal to $J$. The term proportional to $J_{\text{PNC}}$ induces a small mixing between the $|S\rangle$ and $|T_0\rangle$ states. If an oscillating electric field is applied, the term proportional to $J_{\text{PNC}}$ can be modulated at a frequency $\omega$:

$$\hat{H} = 2\pi J \hat{I} \cdot \hat{S} + 2\pi \frac{i \cos(\omega t + \phi) J_{\text{PNC}}}{2} (\hat{I}^+ \hat{S}^- - \hat{I}^- \hat{S}^+). \quad (16)$$

We transform into an interaction frame defined by [32]:

$$\hat{\rho}(t) = e^{-i(\omega t + \phi)I \cdot S} \hat{\rho}(t) e^{i(\omega t + \phi)I \cdot S} \quad (17)$$

where $\hat{\rho}$ is the density operator for the spins and $\phi$ is the phase of the AC electric field. The resulting effective Hamiltonian is:

$$\hat{H} = \Delta \hat{I} \cdot \hat{S} + \frac{i J_{\text{PNC}}}{2} (\hat{I}^+ \hat{S}^- - \hat{I}^- \hat{S}^+), \quad (18)$$

where $\Delta = J - \omega$. Note that this simple form of the Hamiltonian is valid for two spin-1/2 nuclei, a more general treatment is given in Ref. [32]. When $\Delta = 0$ the $|S\rangle$ and $|T_0\rangle$ states undergo an avoided crossing in the interaction frame, mixing to form the states $|\tilde{\alpha}\rangle = \frac{1}{\sqrt{2}}(|S\rangle + i|T_0\rangle)$ and $|\tilde{\beta}\rangle = \frac{1}{\sqrt{2}}(|T_0\rangle + i|S\rangle)$, with a gap equal to $2\pi h J_{\text{PNC}}$ (Figure 1h). While the relaxation times of nuclear spins at zero-field can be 10s of seconds or more [33], the relatively small value of $J_{\text{PNC}}$ means the avoided crossing will be obscured by lifetime broadening. We choose to operate at $\Delta = \pm 1\text{Hz}$, which will give signals with a well-defined frequency as discussed below.

Our proposed experiment involves excitation of magnetization along the y-axis. An experimentally realizable initial condition is:

$$\hat{\rho}(0) = \frac{1}{4} + \frac{B_y h}{4kT} \left[ \frac{\gamma_1 + \gamma_S}{2} (-\hat{I}_y + \hat{S}_y) + \frac{\gamma_1 - \gamma_S}{2} (-\hat{I}_y - \hat{S}_y) \right], \quad (19)$$

which corresponds to magnetizing the spins along the y-axis in a field of strength $B_y$ at a temperature $T$. $k$ is Boltzmann’s constant. Following prepolarization, the sample is suddenly transported to zero field and spin $I$ is inverted to generate a coherent superposition of the $|S\rangle$ and $|T_{\pm 1}\rangle$ states. When $J_{\text{PNC}} = 0$, the magnetization oscillates along the y-axis without any component along the x-axis (Figure 1i). When $J_{\text{PNC}} \neq 0$, the mixing between the $|S\rangle$ and $|T_0\rangle$ generates a signal along the x-axis oscillating at the offset frequency $\Delta$ (Figure 1i). To a first-order approximation, the ratio of the PNC signal to the parity conserving signal is [27]:

$$\frac{4\gamma_1 H \gamma_{19}F \tilde{\upsilon}_{\text{PNC}}}{(\gamma_1^2 H - \gamma_{19}^2 F) \Delta} = 2.7 \times 10^{-5}. \quad (20)$$

Here we report a simulation of the PNC-dependent signal from $^1$H$^{19}$F. We assume the spins are pre-magnetized in a field $B_y = 20\text{ T}$ at 300 K. The simulated sample is $10^{21}$ molecules (100 µL) at a distance of 5 mm from the magnetometer cell, which is typical of zero field NMR detection. Figure 31 shows the time evolution of the magnetic field at the magnetometer cell, which has an amplitude of $\approx 4 \times 10^{-17}\text{T}$. Given a magnetometer sensitivity
of $1.5 \times 10^{-14} \frac{T}{\text{m}}$ [31], this will require 38 hours of signal averaging to achieve a signal to noise ratio greater than unity. We emphasize that this level of signal corresponds to readily-accessible laboratory conditions similar to that in zero-field spectrometers currently in use [31, 35].

Our method has the advantage that the PNC signal will emerge at the offset frequency $\Delta$, which is different than the parity conserving NMR signal at frequency $J$ or the driving electric field at frequency $\omega$. Therefore, while there are a number of systematic errors that could create non-PNC signal along the x-axis (misaligned detector, pulse imperfection, stray fields, etc.) we only need to consider those which involve interference between the frequencies $J$ and $\omega$ and generate some component at $\Delta$ which could mimic the PNC signal. We therefore consider imperfections arising from the AC electric field ($E_{AC}$) and AC magnetic fields ($B_{AC}$) generated by the electrodes. Without yet considering the physical origin of the systematic errors, we include the possibility that they can be even or odd with respect to reversal of the driving field. Table I shows the effects of the available reversals ($\Delta, B_P$, and $E$) on each of these imperfections. We can choose for reversal of $\Delta$ to give an even or odd response by controlling the phase of the AC driving field (i.e. choose a cosine or sine). See Supplemental Material for an analytical, first-order solution demonstrating this dependence. However, the product of the electric and magnetic field response is always even with respect to reversal of $\Delta$, so by choosing a $\Delta$-odd response, systematics involving the product of $B_{AC}$ and $E_{AC}$ can be reversed. Therefore, we are concerned with $E$-odd responses to $B_{AC}$ and $E_{AC}$ that can mimic the PNC signal. For two coupled spins-1/2, the only coupling to an electric field is through the molecular orientation and alignment. One consequence of this is the desired PNC signal. The other is residual dipole-dipole couplings between the two spins. However, this interaction is $E$-even and we can identify no other contribution to the $E_{AC}$ response. The $B_{AC}$ response, however, gives cause for concern. Because of the differing gyromagnetic ratios of the two nuclei, an AC magnetic field along the z-axis can drive the same transition as the PNC interaction and we must estimate its magnitude. We can estimate the maximum value of this field from Ampere's law: $\nabla \times B = \mu_0(J + e_0 \frac{\partial E}{\partial t})$. Assuming an electric field of 60 kV/cm oscillating at 500 Hz, then $\nabla \times B \sim 3 \times 10^{-8} \frac{T}{m}$. Assuming the electric field is supplied by parallel plates with radius of 5 mm, the AC magnetic field should be no more than $2 \times 10^{-10}$ T. The magnitude of the matrix element for the singlet-triplet transition is then [32] $2.5 \times 10^{-4}$ Hz, which is about two orders of magnitude larger than the PNC interaction. This represents a worst-case scenario, in fact $B_{AC}$ will be orthogonal to the z-axis, and will average to zero over a cylindrically symmetric sample, so. Even neglecting this cancellation, if the misalignment of the electrodes is less than $\approx 0.01$ radian, the maximum value of $B_{AC}$ will give a response less than the PNC signal. We note that the magnitude of $B_{AC}$ could be determined from the (non-PNC) NMR response of a reference molecule mixed with the HF and the effects of $B_{AC}$ on HF could be measured separately from the PNC signal by application of a magnetic field from an inductive loop.

In conclusion, the nuclear spin dependent parity non-conserving contribution to the $J$-coupling Hamiltonian in diatomic molecules puts observation of molecular PNC within the reach of current atomic vapor cell magnetometers, even for molecules containing relatively light atoms.

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
PNC effect and imperfections & Reversal & $\Delta$ & $B_P$ & $E$ \\
\hline
PNC & & $\pm$ & $-$ & $-$ \\
$B_{AC}$ (E Odd) & & $\pm$ & $-$ & $-$ \\
$B_{AC}$ (E Even) & & $\pm$ & $+$ & $-$ \\
$E_{AC}$ (E Odd) & & $\pm$ & $-$ & $-$ \\
$E_{AC}$ (E Even) & & $\pm$ & $+$ & $-$ \\
$B_{AC}E_{AC}$ (E Odd) & & $+$ & $-$ & $-$ \\
$B_{AC}E_{AC}$ (E Even) & & $+$ & $+$ & $-$ \\
\hline
\end{tabular}
\caption{Summary of sign change of signal generated at frequency $\Delta$ under reversal of $\Delta, B_P$, or $E$ for PNC effect and imperfections.}
\end{table}

FIG. 1. Detection of $J_{PNC}$ with zero-field NMR: a) Schematic of the zero-field NMR experiment, the spins are prepared in an initial state magnetized along the y-axis, and will give an oscillating magnetization along the y-axis independent of $J_{PNC}$. An AC electric field is applied along the z-axis and a PNC-dependent signal emerges along the x-axis. b) The mixing of the singlet and $T_0$ states can be represented in a time-dependent interaction frame oscillating at the frequency of the AC field. When $\Delta = 0$, an avoided crossing is induced by $J_{PNC}$. Our proposed experiment involves observing singlet-triplet coherences (vertical arrows) when $\Delta \neq 0$ in order to generate an oscillating signal. c) Simulated y-magnetization showing parity conserving signal at frequency $J$. d) Simulated x-magnetization for $^1H$:$^19F$ using the known value of the scalar $J$-coupling and our predicted value for $J_{PNC}$. 

\begin{align*}
\text{TABLE I. Summary of sign change of signal generated at frequency } \Delta \text{ under reversal of } \Delta, B_P, \text{ or } E \text{ for PNC effect and imperfections.}
\end{align*}

\begin{align*}
\begin{array}{|c|c|c|c|}
\hline
\text{PNC effect and imperfections} & \text{Reversal} & \Delta & B_P & E \\
\hline
\text{PNC} & & \pm & - & - \\
\text{B}_{AC} \text{ (E Odd)} & & \pm & - & - \\
\text{B}_{AC} \text{ (E Even)} & & \pm & - & + \\
\text{E}_{AC} \text{ (E Odd)} & & \pm & - & - \\
\text{E}_{AC} \text{ (E Even)} & & \pm & - & + \\
\text{B}_{AC}E_{AC} \text{ (E Odd)} & & + & - & - \\
\text{B}_{AC}E_{AC} \text{ (E Even)} & & + & - & + \\
\hline
\end{array}
\end{align*}
such as HF. The main systematic error will be the generation of AC magnetic fields that could give singlet-triplet spin transitions and mimic the PNC signal. However, with proper design of electrodes the magnitude of the systematic error can be reduced below the level of the PNC signal. We note that this method should also work for more complicated molecules, as long as they have appropriate symmetry.

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SUPPLEMENTAL MATERIAL

Symmetry Rules for Rank-1 J-Couplings

Since we will be considering molecules oriented by an external electric field, the relevant parameter in our proposed experiments is the projection of $J^{(3)}_{PNC}$ along the molecular electric dipole vector. We seek candidate molecules that have a symmetry-allowed $J^{(1)}_{PNC}$ along the dipole but with no parity conserving $J^{(1)}_{PC}$ along the same
axis. \( J^{(1)}_{PC} \) arises in second-order perturbation theory as a product of hyperfine interactions with each nucleus. This product is necessarily even parity and therefore \( J^{(1)}_{PC} \) is a pseudovector. As we will show later, \( J^{(1)}_{PNC} \) results from a cross-term between a nuclear spin dependent weak interaction and a hyperfine interaction. These terms have opposite parity which results in an overall odd parity polar vector \( J^{(1)}_{PNC} \). We can therefore distinguish between \( J^{(1)}_{PNC} \) and \( J^{(1)}_{PC} \) on the basis of parity in molecules whose symmetry point groups contain improper symmetry elements (improper rotations, reflections, and inversion). Molecules that satisfy our criteria belong to the point groups: \( C_n, C_{2n}, \) and \( C_{nv} \) with the further restriction that the two atoms under consideration are not exchanged by symmetry operations [36]. \( C_n \) molecules can have both \( J^{(1)}_{PNC} \) and an electric dipole within the symmetry plane, while \( C_{2n} \) and \( C_{nv} \) molecules have both along the rotational symmetry axis (Figure S1).

![FIG. S1. Symmetry rules for PNC-dependent J-coupling: The molecular point groups for which symmetry-allowed components \( J^{(1)}_{PNC} \) and \( J^{(1)}_{PC} \) can be different are shown schematically. Red arrows indicate symmetry-allowed components while gray arrows indicate symmetry-forbidden components. The symmetry rules shown here are valid only when the two atoms under consideration are not exchanged by a molecular symmetry operation and when \( n > 1 \) for \( C_n \) molecules. By choosing a molecule with the proper symmetry, we can obtain a symmetry-allowed component of \( J^{(1)}_{PNC} \) along the electric dipole without any symmetry-allowed parity conserving components.](image)

**Relativistic Corrections**

Equation. [10] assumes the nonrelativistic limit, but for heavy atoms relativistic effects may be important. The relativistic analogue of Equation 3 is [37]

\[
\hat{H}_{PV} = \frac{G}{\sqrt{2}} \sum_{i,K} g_K \alpha_i \hat{\rho}_K (\mathbf{r}_i - \mathbf{R}_K),
\]

where \( \alpha \) is the Dirac matrix and \( \rho_K (\mathbf{r}) \) is the density of the valence nucleon in the nucleus \( K \). This operator does not contain the electron momentum \( p \) and is not changed in an external magnetic field. Therefore, there is no first-order contribution to the \( J \)-coupling and we need to calculate the second-order cross term between \( \hat{H}_{PV} \) and the parity-even magnetic hyperfine interaction [38]:

\[
\hat{H}_{HF} = \sum_{i,K} \gamma_K \frac{\mathbf{I}_K \cdot \alpha_i \times (\mathbf{r}_i - \mathbf{R}_K)}{(\mathbf{r}_i - \mathbf{R}_K)^3}.
\]

In the sum over intermediate states \( i \) we include both positive (electron) and negative (positron) energy states. In the sum over negative energy states we can approximately substitute energy denominators with a constant \( 2mc^2 \) and after that use closure [?]. This leads us to the effective operator analogous to the second term in Equation 5 which is bilinear in nuclear spin operators and where the \( \delta \)-function is replaced by the nuclear density \( \rho_K \). For heavy atoms, the electron density at the origin \( \rho_e \) is enhanced over the nonrelativistic approximation by a factor [15]:

\[
F_{rel} = \frac{2(1 + \gamma)(2ZR_{nuc})^{2\gamma - 2}}{\Gamma^2(2\gamma + 1)} , \quad \gamma = \sqrt{1 - (\alpha Z)^2}.
\]

Here \( \Gamma(x) \) is gamma-function and \( R_{nuc} \) is nuclear radius in atomic units. This factor is close to unity for \( Z \lesssim 20 \) and then rapidly grows. For example, the nuclei \( ^{88}\text{Sr}^{38} \), \( ^{137}\text{Ba}^{56} \), \( ^{203}\text{Ti}^{81} \), and \( ^{226}\text{Ra}^{88} \) give \( F_{rel} = 1.64, 2.75, 7.64, \) and 10.9 respectively.

**Electric Field Orientation**

The residual rank-1 coupling for a molecule oriented in an electric field is [39]:

\[
\bar{J}^{(1)} = \frac{\mu E}{3kT} J^{(1)},
\]

where \( \mu \) is the electric dipole moment, \( E \) is the electric field experienced by the sample, \( k \) is the Boltzmann constant, and \( T \) the temperature. The scaling is thus given by \( \mu E/3kT \). In polar liquids \( E \) is related to the applied electric field as \( E \approx \left( (\epsilon_r + 2)/3 \right) E_{\text{applied}} \), where \( \epsilon_r \) is the static relative permittivity of the medium. For HF, \( \mu = 2.5 \) D, and \( \epsilon_r = 86 \). Assuming a temperature of 300 K and a field of 60 kV/cm, the orientation scaling factor is 0.09.

**Analytical Calculation of NMR Signal**

As shown in Ref. [27], in the case of a static electric field the time-dependent component of the signal along the x-axis is to a first-order approximation:
\[ \langle M_x(t) \rangle = \frac{4\gamma I\gamma SJ^{(1)}}{N^2J} \cos(Jt), \quad (25) \]

With an AC electric field, we transform into the interaction frame where \( J \) is replaced by \( \Delta \) and \( M_x \) with \( \tilde{M}_x \):

\[ \langle \tilde{M}_x(t) \rangle = \frac{4\gamma I\gamma SJ^{(1)}}{N^2\Delta} \cos(\Delta t + \phi) \]. \quad (26) \]

Finally, we recognize that the \( J^{(1)} \)-dependent signal depends on an admixture of the \( |T_0 \rangle \) state with \( |S \rangle \), and it is \( |T_0 \rangle \langle T_{\pm 1} | \) matrix elements that give rise to the \( x \)-magnetization. These operators commute with \( U(t) \), and therefore \( M_x = \tilde{M}_x \) within the subspace of interest, giving:

\[ \langle M_x(t) \rangle = \frac{4\gamma I\gamma SJ^{(1)}}{N^2\Delta} \cos(\Delta t + \phi) \]. \quad (27) \]

By inspection we can see that \( \langle M_x(t) \rangle \) is odd with respect to reversal of \( \Delta \) when \( \phi = 0^\circ \) or \( \phi = 180^\circ \) and even when \( \phi = 90^\circ \) or \( \phi = 270^\circ \).