Fit functions for the nonlinear hyperfine pressure shifts of alkali-metal atoms

Bart H. McGuyer

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Update: Please see Ref. 1 for an improved, published version of this technical note.

TL;DR: Derivation of fit functions for the dependence of the microwave resonant frequencies of ground-state alkali-metal atoms like Rb on the pressure of Ar, Kr, or Xe buffer gas in vapor cells. Includes the effects of dipolar and quadrupolar hyperfine interactions in short-lived van der Waals molecules not treated in previous work that may account for experimental discrepancies.

CONTENTS

I. INTRODUCTION

My dissertation [2] presents measurements of the 0–0 pressure shifts of both ^{87}Rb and ^{85}Rb in Ar, Kr, and Xe buffer gas [3]. These shifts are nonlinear with pressure presumably because of short-lived van der Waals molecules, each made of an alkali-metal atom weakly bound to a noble-gas atom. Chapter 4 presents a theoretical model that accounts for the ^{87}Rb data [4]. However, that model clearly fails for the data of ^{85}Rb in Xe. In the end, Chapter 4 suggests an improved model is needed that considers additional spin interactions in the molecules.

This note presents a detailed derivation of a candidate for such an improved model. It expands the previous model to include the next two interactions suspected to contribute: the dipolar and quadrupolar hyperfine interactions [5]. However, it differs significantly in its derivation, because expanding the previous model's approach

of treating the bound alkali-metal atom as a weakly perturbed atom suffers quantization issues, despite giving nearly the same results as presented here [6]. The new model uses a more straightforward molecular spin eigenstate approach that surprisingly avoids these issues by including rotation in the eigenstates before taking a classical limit, instead of semi-classically in the interactions [7, 8]. This approach also introduces small corrections for the spin-rotation and Zeeman interactions. The model is able to account for the shape of the nonlinearity observed with ^{85}Rb in Xe [6].

II. DERIVATION

A. Setup

In the time between collisions, a free alkali-metal atom evolves according to a ground-state spin Hamiltonian

$$H_0 = A\,\mathbf{I} \cdot \mathbf{S} - \boldsymbol{\mu} \cdot \mathbf{B}, \tag{1}$$

where the first term is a Fermi-contact interaction coupling the nuclear spin $\mathbf{I}$ and electronic spin $\mathbf{S}$ with a magnetic-dipole coupling coefficient A. The second term is a Zeeman interaction of the total magnetic-dipole moment $\boldsymbol{\mu} = -g_S\mu_B\mathbf{S} + g_I\mu_N\mathbf{I}$ with an externally applied magnetic field $\mathbf{B}$ of amplitude $B = |\mathbf{B}|$. Here, g_S is the electronic g factor, μ_B is the Bohr magneton, g_I is the nuclear g factor, and μ_N is the nuclear magneton. Let us assume that any external field is static and oriented along the lab-frame Cartesian unit vector $\mathbf{z}$, such that $\mathbf{B} = B\mathbf{z}$.

For atomic clocks, the field B is typically weak enough that the dominant interaction in H_0 is the hyperfine coupling. The ground-state energy eigenstates are very nearly the eigenstates $|F\,m\rangle$ of the total spin angular momentum $\mathbf{F} = \mathbf{I} + \mathbf{S}$ with quantum number F and azimuthal quantum number m along $\mathbf{z}$. The hyperfine coupling splits the sublevels into upper and lower hyperfine manifolds with total angular momentum

$$F = \begin{cases} a = I + 1/2, \\ b = I - 1/2, \end{cases} \tag{2}$$

respectively. The nuclear spin I and electronic spin $S = 1/2$ are good quantum numbers for these sublevels.

Vapor-cell clocks measure transitions between these hyperfine manifolds. To proceed, let us consider an "α–β" hyperfine transition between the free-atom eigenstates

$$|\alpha\rangle = |a\,\alpha\rangle \quad \text{and} \quad |\beta\rangle = |b\,\beta\rangle. \tag{3}$$

The 0–0 (or "clock") transition is conventionally used, since it has no first-order dependence on the field B. Ideally, without collisions, the measured resonant frequency would be the Bohr angular frequency for the transition,

$$\omega_{\alpha\beta} = (E_{a\alpha} - E_{b\beta})/\hbar, \tag{4}$$

where $\hbar$ is the reduced Planck constant and the energies $E_{Fm} = \langle F\,m|H_0|F\,m\rangle$. These frequencies are approximately

$$\omega_{\alpha\beta} \approx \frac{A[I]}{2\hbar} + \frac{g_S\mu_B B}{[I]\hbar}(\alpha + \beta), \tag{5}$$

to first order in the field B and ignoring the small Zeeman interaction with the nuclear spin. Here and subsequently, the shorthand

$$[J] = 2J + 1 \tag{6}$$

of brackets about a single quantum number denotes its spin multiplicity.

B. Pressure shifts from sticking collisions

We can calculate the pressure shift from molecule-forming (or sticking) collisions using a density-matrix approach as follows. The density operator ρ for ground-state alkali-metal atoms evolves according to

$$\frac{\partial\rho}{\partial t} = -\frac{i}{\hbar}[H_0, \rho] + \left\langle \frac{1}{T}\left(S\rho S^\dagger - \rho\right)\right\rangle, \tag{7}$$

which for simplicity ignores the effects of optical pumping as well as binary and other non-sticking collisions. The first term on the right models free-atom evolution. The second term models sticking collisions with angle brackets denoting an ensemble average over molecules and their formation rates $1/T$. S is a scattering-matrix operator that captures bound-atom evolution by converting the wave function of a free atom into that of a free atom just exiting a collisional perturbation, following Ch. 10 of [9]. For a particular molecule with lifetime τ, the S-matrix is

$$S = \exp(-i\overline{H}_1\tau/\hbar)\exp(iH_0\tau/\hbar), \tag{8}$$

where $\overline{H}_1$ is the spin Hamiltonian for the bound-atom evolution. Here and subsequently, a bar denotes bound-atom quantities.

The bound-atom spin Hamiltonian $\overline{H}_1$ includes additional interactions that only contribute during the time spent in the molecule. For Rb, the most significant interactions are expected to be the hyperfine-shift (hfs), electronic spin-rotation (sr), dipolar-hyperfine (dh), and quadrupolar-hyperfine (qh) interactions,

$$\overline{H}_1 \approx H_0 + V_{\text{hfs}} + V_{\text{sr}} + V_{\text{dh}} + V_{\text{qh}}, \tag{9}$$

which are addressed below [5]. Other interactions are present but assumed negligible, such as the nuclear spin-rotation and octupole-hyperfine interactions. Interactions with spins in the bound partner like spin exchange are present, but measurements with different Xe isotopes in [2] suggest they are negligible for typical buffer gases. This may no longer apply if, for example, the buffer gas is spin polarized.

In an ideal experiment, the measured α–β frequency is equal to the precession frequency of the coherence $\langle\alpha|\rho|\beta\rangle$. In the secular approximation, molecules from sticking collisions produce a pressure shift

$$\Delta\nu = -\text{Im}\left\langle \frac{\langle\alpha|S|\alpha\rangle\langle\beta|S^\dagger|\beta\rangle}{2\pi T}\right\rangle \tag{10}$$

of the temporal frequency of this coherence as well as a corresponding damping [2]. As before, angle brackets denote averaging over molecules.

For a given rovibrational state, the lifetime is expected to follow an exponential distribution with mean τ. We can average over molecular lifetimes by integrating $\int_0^\infty e^{-t/\tau}\Delta\nu\,dt/\tau$ after introducing bound-atom spin eigenstates $|\overline{\mu}\rangle$ of $\overline{H}_1$ with energies $E_{\overline{\mu}} = \langle\overline{\mu}|\overline{H}_1|\overline{\mu}\rangle$. Averaging then reduces the shift (10) to a sum over bound-atom states

$$\Delta\nu = \sum_{\overline{\mu},\overline{\nu}}\left\langle \frac{|\langle\alpha|\overline{\mu}\rangle\langle\overline{\nu}|\beta\rangle|^2\,(\omega_{\overline{\mu}\,\overline{\nu}} - \omega_{\alpha\beta})\tau}{2\pi T\left[1 + (\omega_{\overline{\mu}\,\overline{\nu}} - \omega_{\alpha\beta})^2\tau^2\right]}\right\rangle, \tag{11}$$

where the bound-atom Bohr frequencies are

$$\omega_{\overline{\mu}\,\overline{\nu}} = (E_{\overline{\mu}} - E_{\overline{\nu}})/\hbar. \tag{12}$$

Here, as with $\overline{H}_1$, a bar denotes bound-atom quantities.

Eq. (11) is the nonlinear pressure shift from molecules. Its rough dependence on buffer-gas pressure p follows from noting that the three-body formation rate $1/T \propto p^2$ and the collision-limited lifetime $\tau \propto 1/p$. At low pressures there is no shift, $\lim_{p\to 0}\Delta\nu \propto p^3$, but at high pressures there is a linear shift, $\lim_{p\to\infty}\Delta\nu \propto p$. Thus, the rough shape of $\Delta\nu$ with pressure is a gradual turning on of a linear shift, with the detailed shape in between sensitive to molecular parameters. One interpretation of the shape of $\Delta\nu$ versus the inverse lifetime $1/\tau \propto p$ is as an interference pattern formed by all of the ways that an α–β coherence may connect through a temporary molecule via discrete $\overline{\mu}$–$\overline{\nu}$ pathways, the interference of which depends on τ.

In measurements, the dominant linear shift is typically that from binary collisions instead of sticking collisions [10]. Therefore, it is convenient to artificially separate the molecular shift into linear and nonlinear parts,

$$\Delta\nu = s_{\text{m}}\,p + \Delta^2\nu, \tag{13}$$

to highlight the nonlinearity that is due to sticking collisions. Here, the infinite-pressure linear slope is

$$s_{\mathrm{m}} = \lim_{p \longrightarrow \infty} \Delta\nu/p$$
$$= \sum_{\overline{\mu},\overline{\nu}} \left\langle \frac{|\langle\alpha|\overline{\mu}\rangle\langle\overline{\nu}|\beta\rangle|^2 (\omega_{\overline{\mu}\,\overline{\nu}} - \omega_{\alpha\beta})\tau}{2\pi T p} \right\rangle, \qquad (14)$$

and the remaining nonlinear shift is

$$\Delta^2\nu = \Delta\nu - s_m\, p$$
$$= -\sum_{\overline{\mu},\overline{\nu}} \left\langle \frac{|\langle\alpha|\overline{\mu}\rangle\langle\overline{\nu}|\beta\rangle|^2 (\omega_{\overline{\mu}\,\overline{\nu}} - \omega_{\alpha\beta})^3\tau^3}{2\pi T\,[1 + (\omega_{\overline{\mu}\,\overline{\nu}} - \omega_{\alpha\beta})^2\tau^2]} \right\rangle. \quad (15)$$

By construction, the nonlinear shift is zero at infinite pressure, $\lim_{p\to\infty} \Delta^2\nu \to 0$, and as a result, is linear at low pressure, $\lim_{p\to0} \Delta^2\nu = -s_{\mathrm{m}}p$. To avoid confusion, note that this nonlinear shift is not an actual pressure shift, but instead is only a convenience for analyzing experiments. The true nonlinear pressure shift is the total molecular shift $\Delta\nu$ of (11). We will focus on the nonlinear pressure shift $\Delta\nu$ below and return to the linear, limiting slope s_{m} of (14) and nonlinear shift $\Delta^2\nu$ of (15) to construct fitting functions.

To calculate these shifts, what remains is to determine the bound-atom eigenstates $|\overline{\mu}\rangle$ and their energies $E_{\overline{\mu}}$ and to average over rovibrational states, their formation rates, and their directions of rotation.

C. Introducing molecular spin eigenstates

To determine the bound-atom eigenstates $|\overline{\mu}\rangle$, we must choose how to treat molecular rotation. Previous work [2, 6] approximated rotation semi-classically in the interactions and thus separately from quantum spins. However, the derivation of (11) with an S-matrix requires $|\overline{\mu}\rangle$ to be energy eigenstates. While bound, the true energy eigenstates are the molecular spin eigenstates formed by the coupling of alkali-metal atomic spins with molecular rotation. Therefore, we will include rotation quantum mechanically in the molecular spin states, connect them with the bound-atom spin states, and then take a classical large-rotation limit. The energies for the interactions considered agree to leading order for both approaches, but their interpretation with respect to quantization is different.

The molecules of interest are loosely bound heteronuclear diatomic molecules in their electronic ground states, composed of a $^1S_0$ noble-gas atom and a $^2S_{1/2}$ alkali-metal atom, with molecular term symbol $X\ ^2\Sigma^+$. Their total electronic spin angular momentum $\mathbf{S}$ is solely due to the alkali-metal atom, so the quantum number $S = 1/2$. Their total orbital angular momentum $\mathbf{L} = 0$, with axial component $\Lambda = 0$, so these molecules follow Hund's case $(b_{\beta S})$ with their electronic spin not strongly coupled to the internuclear axis [11]. The total rotational angular

momentum of the nuclei is $\mathbf{N}$ with quantum number N. As discussed above, we will ignore the nuclear spin from the noble-gas atom.

The strongest spin interaction by far is expected to be the Fermi-contact hyperfine coupling between $\mathbf{I}$ and $\mathbf{S}$, just as for the free alkali-metal atoms, so the resultant $\mathbf{F} = \mathbf{I} + \mathbf{S}$ is still a good quantum number. The total angular momentum for the molecule is then the resultant $\mathbf{G} = \mathbf{F} + \mathbf{N}$. Note that here, and subsequently, the definitions of $\mathbf{F}$ and $\mathbf{G}$ are intentionally swapped compared to those in Brown and Carrington [11], so that $\mathbf{F}$ has the same definition for both ground-state atoms and molecules.

As will be shown below, the Zeeman interaction with $\mathbf{B}$ in (1) sets the quantization axis for the molecules, just as for free atoms. The remaining spin-rotation, dipolar-hyperfine, and quadrupolar-hyperfine interactions do not depend on m_G, just as the spin-orbit, dipolar-hyperfine, and quadrupolar-hyperfine interactions in excited alkali-metal atomic spin states do not depend on the total m. Thus, for moderate applied magnetic fields or less, the molecular spin eigenstates are very nearly the eigenstates

$$|ISF; FNG; G\, m_G\rangle \qquad (16)$$

of the total spin angular momentum $\mathbf{G}$ with quantum number G and azimuthal quantum number m_G along $\mathbf{z}$, in the notation of Brown and Carrington [11]. As will be shown below, G plays the role of $\overline{m}$ in a rotated, bound-atom spin state, connecting this with previous work. For convenience, let us use the shorthand

$$|FNG\, g\rangle = |ISF; FNG; G\, g\rangle \qquad (17)$$

with $g = m_G$, when the values of I, S, and N are understood. Note that for sufficiently strong applied magnetic fields, there will be mixing between G states, just as between F states for free atoms.

To use these molecular eigenstates, first replace the bound-atom eigenstates in (11) with the substitutions

$$|\overline{\mu}\rangle \longrightarrow |F = a, N, G, g\rangle \qquad (18)$$
$$|\overline{\nu}\rangle \longrightarrow |F' = b, N, G', g'\rangle \qquad (19)$$
$$\sum_{\overline{\mu}} \sum_{\overline{\nu}} \longrightarrow \sum_{G,g} \sum_{G',g'}, \qquad (20)$$

where (3) set F and F'. Then, replace the Bohr frequencies (12) and bound-atom energies with the substitutions

$$\omega_{\overline{\mu}\,\overline{\nu}} \longrightarrow \omega_{Gg;G'g'} = (E_{|aNGg\rangle} - E_{|bNG'g'\rangle})/\hbar \qquad (21)$$
$$E_{\overline{\mu}} \longrightarrow E_{|aNGg\rangle} = \langle aNG\, g|\overline{H}_1|aNG\, g\rangle \qquad (22)$$
$$E_{\overline{\nu}} \longrightarrow E_{|bNG'g'\rangle} = \langle bNG'\, g'|\overline{H}_1|bNG'\, g'\rangle. \qquad (23)$$

Finally, the free-atom spin eigenstates have to be modified to include a tensor product,

$$|\alpha\rangle \longrightarrow |a\,\alpha\rangle \otimes |\psi_N\rangle \qquad (24)$$
$$|\beta\rangle \longrightarrow |b\,\beta\rangle \otimes |\psi_N\rangle, \qquad (25)$$

with a rotational wave function $|\psi_N\rangle$ that will be used below to average over the direction of rotation.

D. Large-N approximation

To simplify the matrix elements in (11), we will take a classical limit of $N \gg 1$, which is justified for the molecules of interest [12, 13]. The molecular spin eigenstates decompose into atomic and rotational parts as

$$|F N G\, g\rangle = \sum_{m,m_N} C^{G\,g}_{Fm,Nm_N} |F\,m\rangle \otimes |N\,m_N\rangle. \quad (26)$$

For large N (and thus large G), the quantum number $F \ll G$ and N, and the Clebsch-Gordon coefficient is approximately (Eq. 8.9.1(1) of [14])

$$\left| C^{G\,g}_{Fm,Nm_N} \right| \approx \delta_{g,m+m_N} \left| d^{(F)}_{m,G-N}(\theta_{Gg}) \right| \quad (27)$$

where the angle between $\mathbf{G}$ and the lab $\mathbf{z}$ axis is

$$\theta_{Gg} = \arccos(2g/[G]). \quad (28)$$

The Wigner "little" d-function [14] is

$$d^{(F)}_{m,\overline{m}}(\theta) = \langle F\,m| \exp(-i\theta F_y)|F\,\overline{m}\rangle \quad (29)$$

where the the azimuthal quantum number

$$\overline{m} = G - N \in [-F, F], \quad (30)$$

is that of an effective bound-atom state $|F\,\overline{m}\rangle$.

Using (26) and (27) with (18) and (19), the matrix elements in (11) simplify to

$$|\langle\alpha|\overline{\mu}\rangle|^2 \longrightarrow \left| d^{(a)}_{\alpha,\overline{\mu}}(\theta_{Gg})\langle\psi_N|N, g-\alpha\rangle \right|^2 \quad (31)$$

$$|\langle\overline{\nu}|\beta\rangle|^2 \longrightarrow \left| d^{(b)}_{\beta,\overline{\nu}}(\theta_{G'g'})\langle\psi_N|N, g'-\beta\rangle \right|^2 \quad (32)$$

for large N. Here, the indices $\overline{\mu} = G - N \in [-a, a]$ and $\overline{\nu} = G' - N \in [-b, b]$, or equivalently G and G', play the role of $\overline{m}$ for rotated, bound-atom spin eigenstates, as in previous work [2].

E. Averaging over the direction of rotation

The rotational wave function $|\psi_N\rangle$ may be decomposed in terms of orthonormal Hund's case (b) rotational spin basis functions $|N\,n\rangle$ with $\Lambda = 0$ as $|\psi_N\rangle = \sum_n B_n|N\,n\rangle$ [11]. Each sticking collision then corresponds to a choice of coefficients B_n. To average over the direction of rotation, we need to determine the statistical weights $\langle B_n B_m^* \rangle$ to use with (11).

To proceed, consider using an operator $\mathcal{R}(\theta, \phi, \psi)$ with Euler angles (θ, ϕ, ψ) to rotate an arbitrary $|\psi_N\rangle$ to a new direction. After this rotation, the coefficients are $B_n(\theta, \phi, \psi) = \sum_m B_m(0,0,0)D^{(N)}_{n,m}(\theta, \phi, \psi)$, where the Wigner "big" D-function $D^{(N)}_{n,m}(\theta, \phi, \psi) = \langle N\,n|\mathcal{R}(\theta, \phi, \psi)|N\,m\rangle$. Averaging uniformly over all

Euler-angle values then gives $\langle B_n B_m^* \rangle = \delta_{n,m}/[N]$ from D-function orthogonality.

Therefore, to average over the direction of rotation, replace the rotational wave function with

$$|\psi_N\rangle \longrightarrow |N\,n\rangle \quad (33)$$

and uniformly average over n. Note that, for large N, $G \approx G' \approx N$ and $g \approx g' \approx n$ in $\Delta\nu$. As a result, the angles $\theta_{Gg} \approx \theta_{G'g'}$ and are approximately continuous. After the substitution (33), this average is then approximately

$$\left\langle \Delta\nu \right\rangle_{\psi_N} = \frac{1}{[N]} \sum_{n=-N}^{N} \Delta\nu \approx \frac{1}{2}\int_{-1}^{1} \Delta\nu\, d\cos(\theta) \quad (34)$$

with a shared angle

$$\theta \approx \theta_{Gg} \approx \theta_{G'g'}. \quad (35)$$

Together with the substitutions (18)–(25), (31), and (32), this makes the nonlinear pressure shift (11)

$$\Delta\nu = \sum_{\overline{\mu},\overline{\nu}} \int_{-1}^{1} \left\langle \frac{f^{\alpha\beta}_{\overline{\mu}\,\overline{\nu}}(\theta)(\omega_{\overline{\mu}\,\overline{\nu}}(\theta) - \omega_{\alpha\beta})\tau}{4\pi T[1 + (\omega_{\overline{\mu}\,\overline{\nu}}(\theta) - \omega_{\alpha\beta})^2\tau^2]} \right\rangle d\cos(\theta),$$
$$(36)$$

where the angular weight functions

$$f^{\alpha\beta}_{\overline{\mu}\,\overline{\nu}}(\theta) = \left| d^{(a)}_{\alpha,\overline{\mu}}(\theta)\, d^{(b)}_{\beta,\overline{\nu}}(\theta) \right|^2 \quad (37)$$

generalize those in Eq. (4.94) of [2]. The Bohr frequencies

$$\omega_{\overline{\mu}\,\overline{\nu}}(\theta) = [E_{|a,N,G=\overline{\mu}+N,g=n+\alpha\rangle}(\theta)$$
$$- E_{|b,N,G'=\overline{\nu}+N,g'=n+\beta\rangle}(\theta)]/\hbar \quad (38)$$

depend on the shared angle θ of (35) and (28) if the energies depend on $n \approx \cos(\theta)[N]/2$ via g or g', which occurs only for the Zeeman interaction as shown below.

F. Single-rovibrational-state approximation

The remaining average to complete is that over all rotational and vibrational states allowed by the alkali-metal–noble-gas interaction potential $V(R)$ [15–18]. This average superposes the differing shifts from each rovibrational state. Unfortunately, there is not enough information available about the spin interactions of interest for this to be tractable or trustworthy. Instead, to proceed we will approximate this average using a single rovibrational state with effective parameters, following previous work. That is, we will assume the average is performed over the parameters, keeping the functional form of the shift unchanged.

In this approximation, the $\Delta\nu$ of (36) becomes

$$\Delta\nu = \left(\frac{1}{4\pi\langle T\rangle}\right) \sum_{\overline{\mu},\overline{\nu}} \int_{-1}^{1} \frac{f^{\alpha\beta}_{\overline{\mu}\,\overline{\nu}}(\theta)\,\phi^{\alpha\beta}_{\overline{\mu}\,\overline{\nu}}(\theta)}{1 + [\phi^{\alpha\beta}_{\overline{\mu}\,\overline{\nu}}(\theta)]^2}\, d\cos(\theta) \quad (39)$$

in terms of averaged molecular phase shifts

$$\phi_{\overline{\mu}\,\overline{\nu}}^{\alpha\beta}(\theta) = \langle [\omega_{\overline{\mu}\,\overline{\nu}}(\theta) - \omega_{\alpha\beta}]\tau \rangle \qquad (40)$$

that generalize $m_{\mu\nu}\phi$ in previous work [2]. The remaining brackets here, and subsequently, denote a rovibrational expectation value assuming a single rovibrational state.

G. Interaction energies and fit parameters

Last, what remains is to evaluate the molecular interaction energies and their fit parameters. The calculations are rather tedious [7], so only the results are summarized here with references to Brown and Carrington [11]. The results agree to leading order in $1/N$ with calculations from a bound-atom approach [6], and include small additional corrections to the spin-rotation and Zeeman energies.

For fitting, it is convenient to use pressure-independent and isotope-independent parameters. Noting that τp is very nearly pressure independent, let us introduce a molecular phase-shift parameter

$$(\phi_{\mu\nu}^{\alpha\beta}(\theta)\,p) = (\phi p)_{\mathrm{hfs}} + (\phi_{\mu\nu}p)_{\mathrm{sr}} + (\phi_{\mu\nu}^{\alpha\beta}(\theta)\,p)_{\mathrm{Z}}$$
$$+ (\phi_{\mu\nu}p)_{\mathrm{dh}} + (\phi_{\mu\nu}p)_{\mathrm{qh}} \qquad (41)$$

with pressure-independent contributions from each interaction to be determined below. Isotope-independent fit parameters for each contribution will be introduced for each. The top line has the contributions from the three interactions previously considered, including the Zeeman (Z) interaction in (1). As shown below, only the Zeeman contribution depends on α, β, and θ. The bottom line has the contributions from the two new interactions not previously considered.

1. Hyperfine-shift interaction (hfs)

The perturbation to the Fermi-contact interaction is modeled by the hyperfine-shift interaction,

$$V_{\mathrm{hfs}} = \delta A(R)\,\mathbf{I} \cdot \mathbf{S}, \qquad (42)$$

where $\delta A(R)$ is a potential that depends on internuclear distance R and is generally expected to change sign at least once for our molecules of interest [2, 5, 19–27]. This interaction is diagonal in G and m_G, and has the same form as the Fermi-contact interaction in (1).

The molecular energies follow Eqs. (10.49) and (11.80) in Brown and Carrington [11] and are the same as those in the atomic case,

$$E_{|FNGg\rangle}^{\mathrm{hfs}} = \langle \delta A(R) \rangle \frac{1}{4} \left\{ (F-b)[b] + (F-a)[a] \right\}, \quad (43)$$

where brackets denote a rovibrational expectation value.

The molecular phase-shift parameter

$$(\phi p)_{\mathrm{hfs}} = \frac{\langle \delta A(R)\,\tau \rangle\,p\,[I]}{2\hbar} = (\psi p)_{\mathrm{hfs}} \frac{g_I[I]}{2} \qquad (44)$$

is independent of μ and ν, and equal to (ϕp) in previous work [2, 4, 28]. For fitting data, the parameter

$$(\psi p)_{\mathrm{hfs}} = \frac{\langle \delta A(R)\,\tau \rangle\,p}{g_I\hbar} \qquad (45)$$

(units of rad Torr) is pressure independent and very nearly isotope independent, because A/g_I is isotope independent up to a part-per-thousand hyperfine anomaly for Rb [29, 30].

2. Spin-rotation interaction (sr)

The electronic spin-rotation interaction is

$$H_{\mathrm{sr}} = \gamma(R)\,\mathbf{S} \cdot \mathbf{N}. \qquad (46)$$

where $\gamma(R)$ is a potential that depends on internuclear distance [5, 9, 31–33]. While the literature gives a general impression that $\langle \gamma(R) \rangle$ should be positive, precision measurements and theory confirm it is negative for LiAr [34, 35]. This interaction can have multiple physical origins [11], but the most significant origin here is expected to be the spin-orbit interaction in the noble-gas atom [31]. This interaction is diagonal in G and m_G.

The molecular energies follow Eqs. (10.48) and (11.85) in Brown and Carrington [11],

$$E_{|FNGg\rangle}^{\mathrm{sr}} = \frac{(-1)^{F-a}\langle \gamma(R) \rangle}{[I]} \left(\overline{m}\langle N \rangle \right.$$
$$\left. + \frac{\overline{m}(\overline{m}+1) - F(F+1)}{2} \right) \qquad (47)$$

where $\overline{m} = G - N$. The first term matches previous work [2]. The second term is a correction of relative order $1/\langle N \rangle$ with a form that roughly resembles the dipolar and quadrupolar energies below.

The molecular phase-shift parameters are

$$(\phi_{\mu\nu}p)_{\mathrm{sr}} = \frac{(\psi p)_{\mathrm{sr}}}{[I]} \left(\mu + \nu \right.$$
$$\left. + \frac{2\mu(\mu+1) + 2\nu(\nu+1) - 4I(I+1) - 1}{4\langle N \rangle} \right) \qquad (48)$$

using a pressure- and isotope-independent parameter

$$(\psi p)_{\mathrm{sr}} = \langle \gamma(R)N\tau \rangle\,p/\hbar \qquad (49)$$

(units of rad Torr). Ignoring the correction, this parameter is equivalent to $r_1\phi p(\mu+\nu) = \lim_{N\to\infty}(\psi_{\mu\nu}p)_{\mathrm{sr}}/[I]$ in previous work [2, 4]. The sign of $(\psi p)_{\mathrm{sr}}$ has an effect only through the small $1/N$ correction term (48), which contributes to both the nonlinear and linear shifts. This correction term depends on $(\psi p)_{\mathrm{sr}}/\langle N \rangle$, so is independent of N in the single-state approximation.

Table II provides estimates of $(\psi p)_{\mathrm{sr}}$.

3. Dipolar-hyperfine interaction (dh)

The electron-nuclear dipolar (or anisotropic hyperfine-shift) interaction can be expressed in many forms [11]. For a strong coupling of $\mathbf{I}$ and $\mathbf{S}$, the most convenient is

$$V_{\text{dh}} = \sqrt{6}g_S\mu_B g_I\mu_N \left(\frac{\mu_0}{4\pi}\right) T^2(\mathbf{C}) \cdot T^2(\mathbf{S},\mathbf{I}), \qquad (50)$$

following the notation of Eq. (1.56) in Brown and Carrington [11], where μ_0 is the vacuum permeability and $T^2(\mathbf{C})$ is a tensor involving the alkali-metal valence electron position about its nucleus. This interaction is diagonal in G and m_G. For reference, using Eq. (5.116) in [11], an effective Hamiltonian for this interaction is

$$V_{\text{dh}} \approx t_0(R)\,\mathbf{I} \cdot (3\hat{R}\hat{R} - \mathbb{1}) \cdot \mathbf{S}, \qquad (51)$$

where the axial magnetic-dipole hyperfine coefficient $t_0(R)$ measures the aspherical symmetry of the Rb valence electronic wavefunction, $\hat{R}$ is the internuclear axis unit vector, and $\mathbb{1}$ is the unity dyadic tensor. The coefficient t_0 is related to the "Frosh and Foley" parameter $c = t_0/3$.

The molecular energies follow Eqs. (1.60), (8.513–8.515), (10.50), and (11.81–11.84) in Brown and Carrington [11]. The derivation includes a Wigner 9j symbol that is available in Table 10.3 of [14]. These energies are

$$E^{\text{dh}}_{|FNGg\rangle} = (-1)^{F-b}\frac{\langle t_0(R)\rangle}{2[I]}$$
$$\times \left\langle \frac{3X_{F,\overline{m}}(X_{F,\overline{m}} - 1) - 4N(N+1)F(F+1)}{(2N-1)(2N+3)} \right\rangle \quad (52)$$

for the quantities

$$X_{F,\overline{m}} = F(F+1) - \overline{m}(\overline{m}+[N]) \qquad (53)$$

and $\overline{m} = G - N$, assuming $I \geq 1/2$. The brackets apply to the remaining dependence on N.

The molecular phase-shift parameters are

$$(\phi_{\mu\nu}p)_{\text{dh}} = \frac{g_I(\psi p)_{\text{dh}}}{2[I]} \left\langle \frac{2N(N+1)[I]^2 - 3Y^+_{\mu,\nu}}{(2N-1)(2N+3)} \right\rangle \quad (54)$$

for the quantity

$$Y^{\pm}_{\mu,\nu} = X_{a,\mu}(X_{a,\mu} - 1) \pm X_{b,\nu}(X_{b,\nu} - 1) \qquad (55)$$

using a pressure- and isotope-independent parameter

$$(\psi p)_{\text{dh}} = \frac{\langle t_0(R)\,\tau p\rangle}{g_I\hbar} \qquad (56)$$

(units of rad Torr). For reference, the leading-order term in a $1/\langle N\rangle$ expansion is

$$(\phi_{\mu\nu}p)_{\text{dh}} \approx g_I(\psi p)_{\text{dh}} \left(\frac{[I]}{4} - \frac{3(\mu^2 + \nu^2)}{2[I]}\right). \qquad (57)$$

The first part resembles the hyperfine-shift interaction and the second part modifies the shape of the nonlinear shift.

Walker and Happer [5] provide an estimate for the strength of this interaction for ^{85}Rb with ^{131}Xe. Noting that the coefficient $t_0(R) = B_a(R)$ in Eq. (31) of [5], Fig. 14 of [5] estimates $|t_0(R)| \leq |\gamma(R)|$ for $R \in [2, 4.5]$ Å, which is just before the potential well in $V(R)$ [15]. Assuming this inequality holds generally for larger R, then it gives a rough estimate of $|(\psi p)_{\text{dh}}| \leq |(\psi p)_{\text{sr}}|/(\langle N\rangle g_I) \approx 0.5$ rad Torr for Rb in Xe using values in Table II.

4. Quadrupolar-hyperfine interaction (qh)

The nuclear electric quadrupole interaction can be expressed in many forms [11]. For a strong coupling of $\mathbf{I}$ and $\mathbf{S}$, the most convenient is

$$V_{\text{qh}} = -e\,T^2(\mathbf{Q}) \cdot T^2(\nabla\mathbf{E}), \qquad (58)$$

following the notation of Eq. (1.28) in Brown and Carrington [11]. Here, Q is the quadrupole moment of the alkali-metal nucleus. This interaction is diagonal in G and mG. For reference, using Eqs. (5.116), (7.158), and (7.192) in [11], an effective Hamiltonian for this interaction is

$$V_{\text{dh}} \approx \frac{eq_0(R)Q}{4I(2I-1)}\,\mathbf{I} \cdot (3\hat{R}\hat{R} - \mathbb{1}) \cdot \mathbf{I}, \qquad (59)$$

where $q_0(R)$ is a standard measure of the electric field gradient along the internuclear axis.

The molecular energies follow a derivation similar to Eq. (9.93) and Appendix 8.4 in Brown and Carrington [11] and uses Eqs. (5.173), (9.13-14), and (7.159) in that reference. These energies are

$$E^{\text{qh}}_{|FNGg\rangle} = \frac{e\langle q_0(R)Q\rangle}{4I(2I-1)} \left(\frac{(-1)^{F-a}}{[I]} - \frac{1}{2}\right)$$
$$\times \left\langle \frac{3X_{F,\overline{m}}(X_{F,\overline{m}} - 1) - 4N(N+1)F(F+1)}{(2N-1)(2N+3)} \right\rangle \quad (60)$$

for $\overline{m} = G - N$ and $X_{F,\overline{m}}$ of (53), assuming $I \geq 1$. The brackets apply to the remaining dependence on N.

The molecular phase-shift parameters are

$$(\phi_{\mu\nu}p)_{\text{qh}} = \frac{3(\psi p)_{\text{qh}}Q}{8I(2I-1)[I]} \left\langle \frac{2Y^+_{\mu,\nu} - [I]Y^-_{\mu,\nu}}{(2N-1)(2N+3)} \right\rangle \quad (61)$$

for the quantities $Y^{\pm}_{\mu,\nu}$ of (55), using a pressure- and isotope-independent parameter

$$(\psi p)_{\text{qh}} = e\,\langle q_0(R)\,\tau p\rangle/\hbar \qquad (62)$$

(units of rad Torr/Barn). For reference, the leading-order term in a $1/\langle N\rangle$ expansion is

$$(\phi_{\mu\nu}p)_{\text{qh}} \approx \frac{3(\psi p)_{\text{qh}}Q}{8I(2I-1)[I]} \left[\nu^2(2I+3) - \mu^2(2I-1)\right]. \qquad (63)$$

This term modifies the shape of the nonlinear shift.

Walker and Happer [5] provide an estimate for the strength of this interaction for ^{85}Rb with ^{131}Xe. Noting that the coefficient $C_a(R) = eq_0(R)Q/\{4I(2I-1)\}$ in Eq. (31) of [5], Fig. 14 of [5] estimates $|C_a(R)| \leq |\gamma(R)/20|$ for $R \in [2, 3.5]$ Å, which is just before the potential well in $V(R)$ [15]. Assuming this inequality holds generally for larger R, then it gives a rough estimate of $|(\psi p)_{qh}| \leq |(\psi p)_{sr}|4I(2I-1)/(20\langle N \rangle Q) \approx 0.5$ rad Torr/Barn for Rb in Xe using values in Table II.

5. Zeeman interaction (Z)

The Zeeman interaction in H_0 and has both nuclear and electronic spin contributions. For simplicity, as in previous work, let us ignore the nuclear contribution. Then the Zeeman interaction is very nearly

$$H_Z = -\boldsymbol{\mu} \cdot \mathbf{B} \approx g_S \mu_B \mathbf{B} \cdot \mathbf{S}. \tag{64}$$

This interaction sets the atomic and molecular quantization axes to be along the applied field $\mathbf{B}$ in the lab frame, so is diagonal in m_G. However, it is not diagonal in G, and for sufficiently large fields B, will induce mixing between low-field eigenstates with different values of G.

The molecular energies follow Eqs. (11.91–92) in Brown and Carrington [11]. For the electronic spin only, the energies are

$$E^Z_{|FNGg\rangle} = (-1)^{F-a} g_S \mu_B B \left(\frac{2g}{[G]} \right)$$
$$\times \left(\frac{[G]}{2} \right) \frac{G(G+1) + F(F+1) - N(N+1)}{2G(G+1)}. \tag{65}$$

The molecular phase-shift parameters are

$$(\phi^{\alpha\beta}_{\mu\nu}p)_Z \approx \frac{g_S \mu_B B \tau p}{[I]\hbar} \left[-\alpha - \beta + \cos(\theta)\left(\mu + \nu \right. \right.$$
$$\left. \left. + \frac{4I(I+1) + 1 - 2\mu^2 - 2\nu^2}{4\langle N \rangle} \right) \right], \tag{66}$$

using (35) and (28) and including only the first and second terms in a $1/N$ expansion. The first term is equivalent to $-(r_1\phi p)(\alpha + \beta)$ in the low-field limit of previous work [2]. The second term is a small correction with a form that roughly resembles the dipolar and quadrupolar energies above.

H. Fitting functions

To analyze data, we fit a data set of α–β transition frequencies $f = f(p)$ measured at different buffer-gas pressures p using a fit function

$$f = \nu_0 + (s_b + s_m)p + \Delta^2\nu \tag{67}$$

TABLE I. Atomic parameters for reference. The values of are calculated from values of $\mu_I = g_I I \mu_N$ in [36]. Note that the ratio $Q(^{87}\text{Rb})/Q(^{85}\text{Rb})$ for free atoms and for molecules like RbCl and RbF differ on the order of one percent [37].

Atom	I	g_I [36]	Q (Barns) [37]
^{85}Rb	5/2	0.541192	0.276 ± 0.001
^{87}Rb	3/2	1.83421	0.1335 ± 0.0005

TABLE II. Molecular parameters for reference from measurements by Bouchiat *et al.* [12, 13]. The values of $(\psi p)_{sr}$ are calculated from the effective spin-rotation magnetic field $B_1 = \langle \gamma N \rangle/(g_S \mu_B)$ as $(\psi p)_{sr} = g_S \mu_B B_1 \langle \tau \rangle p/\hbar$. The values of $\langle N \rangle$ are rough theoretical estimates.

Parameter	RbAr [13]	RbKr [12]	RbXe [12]
$\langle Tp^2 \rangle$ (ms Torr^2)	16.1 ± 1.3	10.6 ± 0.5	4.29 ± 0.23
$\langle \tau p^2 \rangle$ (ns Torr)	48.5 ± 1.9	56.9 ± 1.7	34–61
$(\psi p)_{sr}$ (rad Torr)	1.016 ± 0.040	9.61 ± 0.40	31.9 ± 9.2
B_1 (Gauss)	1.19 ± 0.05	9.59 ± 0.28	38.1 ± 1.6
$\langle N \rangle$	30.5–33.3	41.5	63.2–76.7

with a zero-pressure intercept ν_0, a binary pressure-shift slope s_b, a molecular pressure-shift slope s_m, and a nonlinear pressure shift $\Delta\nu$. The nonlinear shift $\Delta^2\nu$ is more convenient here than $\Delta\nu$ because of its ease of plotting.

The two slopes may be combined into a total linear slope $s = s_b + s_b$. However, it is convenient to use separate slopes to compare isotopes. Note that the expected isotopic scaling of the binary slope is $s_b \propto A[I]$ [2].

In practice, it's convenient to decouple the parameters as follows: Fit the parameter $(\psi p)_n/\sqrt{\langle Tp^2 \rangle}$ instead of $(\psi p)_n$ for $n = $ hfs, sr, dh, and qh (this helps decouple the shape of $\Delta^2\nu$ from its size); Fit the parameter $(\psi p)_n/(\langle N \rangle \langle Tp^2 \rangle)$ instead of $\langle N \rangle$ (this helps with s_m while fitting different isotopes with shared parameters); Last, ignore the hfs contribution to s_m when initially comparing isotopes (this helps decouple s_m and $\Delta^2\nu$).

In experiments, care is needed to remove nonlinearity in pressure measurements, to account for inaccuracy between pressure gauges when comparing slopes, and to constrain the zero-pressure intercept [2].

Tables I and II provide atomic and molecular parameters for reference.

1. Fit function for moderate applied fields

With the above averages and approximations, and for moderate applied field strengths B such that G is still a good quantum number, the nonlinear pressure shift is given by (39) with molecular phase-shift parameters given in (41), (44), (48), (54), (61), and (66).

Re-arranging to use these pressure-independent pa-

rameters, the equivalent linear, limiting slope is

$$s_m = \left(\frac{1}{4\pi\langle Tp^2\rangle}\right) \sum_{\mu,\nu} \int_{-1}^{1} f_{\mu\nu}^{\alpha\beta}(\theta)[\phi_{\mu\nu}^{\alpha\beta}(\theta)p]\, d\cos(\theta),$$
(68)

and the equivalent nonlinear shift is

$$\Delta^2\nu = \left(\frac{-1}{4\pi\langle Tp^2\rangle}\right) \sum_{\mu,\nu} \int_{-1}^{1} \frac{f_{\mu\nu}^{\alpha\beta}(\theta)[\phi_{\mu\nu}^{\alpha\beta}(\theta)p]^3 p}{p^2 + [\phi_{\mu\nu}^{\alpha\beta}(\theta)p]^2}\, d\cos(\theta).$$
(69)

For convenience, here and subsequently, the bar notation is removed in fit functions. The pressure-independent parameter $\langle Tp^2\rangle$ describes the formation of molecules.

2. Fit function for negligible applied fields

For magnetic fields that are small enough to not influence the nonlinear shift significantly while still defining the quantization axis, we may set $B = 0$ such that the phase shifts $\phi_{\mu,\nu}^{\alpha\beta}$ do not depend on θ, then (69) becomes

$$\Delta^2\nu \approx \Delta_2^2\nu = -\left(\frac{1}{2\pi\langle Tp^2\rangle}\right) \sum_{\mu,\nu} \frac{W_{\mu\nu}^{\alpha\beta}(\phi_{\mu\nu}^{\alpha\beta}p)^3 p}{p^2 + (\phi_{\mu\nu}^{\alpha\beta}p)^2}$$
(70)

with a subscript introduced for reference later. The corresponding molecular linear, limiting slope (68) becomes

$$s_m = \left(\frac{1}{2\pi\langle Tp^2\rangle}\right) \sum_{\overline{\mu},\overline{\nu}} W_{\mu\nu}^{\alpha\beta}(\phi_{\overline{\mu}\,\overline{\nu}}^{\alpha\beta}p).$$
(71)

The negligible-field weight coefficients

$$W_{\mu\nu}^{\alpha\beta} = \frac{1}{2}\int_{-1}^{1} f_{\mu\nu}^{\alpha\beta}(\theta)\, d\cos\theta$$
(72)

generalize the $W_\sigma = \sum_\mu W_{\mu;\sigma-\mu}^{00}$ in previous work [2].

The threshold to enter this negligible-field regime depends on the choice of transition and the fit parameter values. Numerically, for the 0–0 transition, this regime seems to occur for $B \lesssim B_1$ for the spin-rotation fields B_1 in Table II. However, the thresholds for some other transitions such as end-state resonances seems to lower.

3. 0–0 transition weights and linear shift

For the 0–0 transition, the weights (72) are

$$W_{\mu\nu} = (-1)^{\mu+\nu} \sum_k \frac{1}{[k]} C_{a0;a,0}^{k0} C_{a\mu;a,-\mu}^{k0} C_{b0;b,0}^{k0} C_{b,\nu;b,-\nu}^{k0}.$$
(73)

where the superscripts α and β are omitted for convenience. Table III gives explicit weights of interest.

TABLE III. Weights (73) for the 0–0 transition with negligible magnetic field versus nuclear spin quantum number. Common alkali-metal atoms are indicated for convenience. The rows correspond to $\mu \in [a, a-1, \dots, 1-a, -a]$, and the columns to $\nu \in [b, b-1, \dots, 1-b, -b]$:

I	$W_{\mu\nu}$
1/2	$\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} / 3$
3/2 (^{87}Rb)	$\begin{pmatrix} 9 & 3 & 9 \\ 6 & 9 & 6 \\ 5 & 11 & 5 \\ 6 & 9 & 6 \\ 9 & 3 & 9 \end{pmatrix} / 105$
5/2 (^{85}Rb)	$\begin{pmatrix} 50 & 20 & 25 & 20 & 50 \\ 30 & 45 & 15 & 45 & 30 \\ 24 & 36 & 45 & 36 & 24 \\ 23 & 29 & 61 & 29 & 23 \\ 24 & 36 & 45 & 36 & 24 \\ 30 & 45 & 15 & 45 & 30 \\ 50 & 20 & 25 & 20 & 50 \end{pmatrix} / 1155$
7/2 (^{133}Cs)	$\begin{pmatrix} 245 & 105 & 105 & 91 & 105 & 105 & 245 \\ 140 & 210 & 84 & 133 & 84 & 210 & 140 \\ 110 & 150 & 204 & 73 & 204 & 150 & 110 \\ 100 & 120 & 180 & 201 & 180 & 120 & 100 \\ 97 & 117 & 141 & 291 & 141 & 117 & 97 \\ 100 & 120 & 180 & 201 & 180 & 120 & 100 \\ 110 & 150 & 204 & 73 & 204 & 150 & 110 \\ 140 & 210 & 84 & 133 & 84 & 210 & 140 \\ 245 & 105 & 105 & 91 & 105 & 105 & 245 \end{pmatrix} / 9009$

The molecular linear slope (71) evaluates to

$$\begin{aligned}
s_m = \frac{[I]}{2\pi\langle Tp^2\rangle} \Bigg(& \frac{g_I(\psi p)_{\mathrm{hfs}}}{2} - \frac{(\psi p)_{\mathrm{sr}}}{6\langle N\rangle} \\
& - \frac{(\psi p)_{\mathrm{dh}}[1 + 2I(I+1)]}{5(2N-1)(2N+3)} \\
& + \frac{(\psi p)_{\mathrm{qh}}[3 - 4I(I+1)]}{20I(2I-1)(2N-1)(2N+3)} \Bigg)
\end{aligned}$$
(74)

for $I \in \{1/2, 3/2, 5/2, 7/2\}$ with the weights shown in Table III. Note that the quadrupolar interaction is not allowed for $I = 1/2$. The first term from the hyperfine-shift interaction shares an isotopic scaling with $s_b \propto [I]A$, so is indistinguishable from s_b except for how parameters are fitted via $\Delta^2\nu$. The second term from the spin-rotation interaction has a different isotopic scaling than s_b, so might be directly distinguishable by comparing isotopes. The remaining contributions from the dipolar and quadrupolar interactions are of second and higher order in $1/\langle N\rangle$ and also have different isotopic scalings.

I. Relation to fit functions in previous work

Previous published work considered only the 0–0 transition with negligible applied fields [4, 28]. We can recover the "low-field spin-rotation" model of [4] from (70) by setting $(\psi p)_{\mathrm{dh}} = 0$, $(\psi p)_{\mathrm{qh}} = 0$, and $\langle N \rangle \longrightarrow \infty$. Using the relation $\sum_\mu W_{\mu,\sigma-\mu} = W_\sigma$, where $\sigma = \mu + \nu$, this recovers the nonlinear shift

$$\Delta_2^2 \to \Delta_1^2 = -\left(\frac{1}{2\pi T}\right) \sum_{\sigma=-2I}^{2I} \frac{W_\sigma (1 + r_1\sigma)^3 \phi^3}{1 + (1 + r_1\sigma)^2 \phi^2} \quad (75)$$

from [2, 4], where $\phi = \delta A[I]\tau/(2\hbar)$ and $r_1 = 2\gamma N/(\delta A[I]^2)$. We can recover the model of [28] by additionally setting $(\psi p)_{\mathrm{sr}} = 0$. Using the property

$\sum_{\mu\nu} W_{\mu\nu} = 1$, this recovers the nonlinear shift

$$\Delta_2^2 \to \Delta_0^2 = -\left(\frac{1}{2\pi T}\right)\frac{\phi^3}{1 + \phi^2}, \quad (76)$$

of [2, 28]. For both of the above models, this also recovers the corresponding molecular linear slope $s_m = (\phi p)_{\mathrm{hfs}}/[2\pi(Tp^2)]$ of all previous work [2].

Previous unpublished work in [2] attempts to capture the effects of moderate applied fields using a bound-atom approach. We recover very nearly the same model by setting $(\psi p)_{\mathrm{dh}} = 0$, $(\psi p)_{\mathrm{qh}} = 0$, and $\langle N \rangle \longrightarrow \infty$. However, the details and interpretation of the angular average in (69) are rather different than that of Eq. (4.98) in [2], except in the limit of small applied fields.

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