Spin squeezing an ultracold molecule

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(Dated: September 21, 2015)

In this article we present a concrete proposal for spin squeezing the ultracold ground state polar paramagnetic molecule OH, a system currently under fine control in the laboratory. In contrast to existing work, we consider a single, non-interacting molecule with angular momentum greater than 1/2. Starting from an experimentally relevant effective Hamiltonian, we identify a parameter regime where different combinations of static electric and magnetic fields can be used to realize the single-axis twisting Hamiltonian of Kitagawa and Ueda [M. Kitagawa and M. Ueda, Phys. Rev. A 47, 5138 (1993)], the uniform field Hamiltonian proposed by Law et al. [C. K. Law, H. T Ng and P. T. Leung, Phys. Rev. A 63, 055601 (2001)], and a model of field propagation in a Kerr medium considered by Agarwal and Puri [G. S. Agarwal and R. R. Puri, Phys. Rev. A 39, 2969 (1989)]. To support our conclusions, we provide analytical expressions as well as numerical calculations, including optimization of field strengths and accounting for the effects of field misalignment. Our results have consequences for applications such as precision spectroscopy, techniques such as magnetometry, and stereochemical effects such as the orientation-to-alignment transition.

PACS numbers: 42.50.Dv, 42.50.Lc, 32.60.+i

I. INTRODUCTION

The ultracold OH molecule is a versatile platform for precision measurements. Its experimental appeal lies in the fact that its ground $X^2\Pi_{3/2}$ state is polar as well as paramagnetic, and is therefore readily manipulated in the laboratory with the use of electric and magnetic fields $\vec{E}$, $\vec{B}$. Applications explored thus far include precision spectroscopy [6,7] and quantum information processing [8], in addition to studies of cold chemistry [9,10] and quantum degeneracy [11].

In this article, we consider spin squeezing of the OH molecule. Our discussion occurs in the context of the Heisenberg uncertainty relation [12]

$$\Delta J_x \Delta J_y \geq |\langle J_z \rangle|/2,$$

(1)

between the three components of the angular momentum operator $J$. Spin squeezing refers to a situation where the fluctuation in one of the components, say $\Delta J_x$, is reduced to below the standard quantum limit $\sqrt{|\langle J_z \rangle|^2/2}$. Of course, the fluctuations in $J_y$ increase correspondingly, in order to maintain the relation of Eq. (1).

Spin squeezing constitutes a technique of interest at the frontiers of precision measurement and has applications in spectroscopy, magnetometry, metrology, the detection of particle correlation and entanglement, and quantum computation and simulation ([15,16] and references therein). The pioneering start to spin squeezing was provided by the work of Kitagawa and Ueda [17,18] and Wineland et al. [19,20], who considered the squeezing of collective atomic spins, and was followed by many investigations [21,59], for example). We emphasize that all of this work relates to ensembles of correlated (pseudo)spins, represented by atoms (in a thermal vapor or a degenerate gas), nuclei [60], or molecules [61], where the collective spin can assume a high value [62].

More recently, squeezing has also been considered for single (atomic or nuclear) spins, or equivalently, for an uncorrelated ensemble of such spins. Experiments have been carried out, using spin 3 [63] and spin 7/2 [64] states of Cesium atoms. Possibilities also exist for Dysprosium which offers states with spins from 8 up to 12.5. Theoretical calculations of single-spin squeezing have been presented as well [65]. The squeezing in this case is limited by the much smaller angular momentum available. Nonetheless, some effects can be experimentally relevant, for example for precision spectroscopy [20]. Motivated by such a consideration, we consider spin squeezing of a single OH molecule. Interesting applications to the measurement of magnetic fields also seem possible [66,70], especially following recent discussions of magnetometry using single SiC spins with angular momentum 3/2 [71]; ground state ultracold OH also carries rotational angular momentum 3/2, and is sensitive to magnetic fields via the Zeeman shift. As well, spin squeezing is related to the alignment-to-orientation transition [62], and we expect this perspective will be of relevance to our work, given the recent interest in the stereochemical properties of the OH molecule [72]. We emphasize that compared to previous proposals for spin squeezing molecules [61], which employ spin 1/2 interacting molecules squeezed collectively, we consider a single noninteracting molecule with angular momentum 3/2.

In present-day laboratories, ultracold OH molecules are typically confined in magnetoelectrostatic traps [2,4,14,73,74]. We therefore consider spin squeezing enabled...
by these readily available static electric and magnetic fields. The advantage of using static, rather than optical or microwave fields, for squeezing is that damping and decoherence due to spontaneous emission can be avoided. Our starting point will be an effective eight-dimensional matrix Hamiltonian that has been shown to model recent OH experiments quite well [14, 73, 74], and has also been diagonalized analytically [75, 76]. We demonstrate that for Zeeman and Stark shifts small compared to the Lambda-doublet splitting of the OH ground state, this Hamiltonian can yield spin-squeezing of the types considered by Kitagawa and Ueda [18], Law et al. [30] and Agarwal and Puri [21]. We provide analytic and numerical results, discuss the optimization of the field strengths, and include the effects of field misalignment in our treatment.

The remainder of this article is arranged as follows. Section II presents the derivation of the spin squeezing Hamiltonian, Section III discusses the dynamics of the squeezing parameter, Section IV addresses the detection of the proposed squeezing, and Section V supplies a conclusion.

II. DERIVATION OF THE SPIN SQUEEZING HAMILTONIAN

A. The eight dimensional effective Hamiltonian

Several experiments on ultracold OH molecules in crossed electric and magnetic fields, see Fig.1, have been successfully modeled using an effective Hamiltonian involving only eight quantum states [73, 74]. The domain of validity of this Hamiltonian and the details of the states involved can be found in several articles [14, 71, 76], and will not be repeated here. This effective Hamiltonian was recently diagonalized analytically following the detection of an underlying chiral symmetry [22]. In the process of identifying that symmetry, it was found that the OH matrix Hamiltonian could be re-expressed in terms of two interacting spins (to avoid notational clutter we set ℏ = 1; to make contact with laboratory parameters, requisite factors of ℏ can be supplied to any formula in this article by inspection, see the example supplied below),

$$ H_M = -\tilde{\Delta}\sigma_z - \tilde{B}J_z + \tilde{E}\sigma_x (J_z\cos \theta - J_x \sin \theta), \quad (2) $$

where the constants are given by

$$ \tilde{\Delta} = \frac{\Delta}{2}, \quad \tilde{B} = \frac{4\mu_B B}{5}, \quad \tilde{E} = \frac{2\mu_e E}{5}, \quad (3) $$

Δ being the Lambda-doublet splitting, B and E the uniform magnetic and electric fields, respectively, μ_B the Bohr magneton and μ_e the electric dipole moment of the OH molecule. In Eq. (2), θ is the angle between the electric and magnetic fields (see Fig. 1), and σ = 1/2 and J = 3/2 are the two interacting spins. The spin σ is a pseudo-spin, with the spin projections σ_z = ±1 and σ_x = 1 corresponding to the two Lambda-doublet manifolds of parity e and f, respectively. On the other hand, J corresponds to the rotation of the molecular axis, and the values J_z = ±1/2, ±3/2 indicate the various projections of J on the laboratory z axis, which is chosen for convenience and without loss of generality to be along the magnetic field. The matrix representation of H_M is reproduced in the appendix for the reader’s convenience, see Eq. (48).

At this point the insertion of factors of ℏ in Eq. (4) may be considered as a useful exercise. We begin with the observation that H_M has units of energy. Since the Pauli matrix σ_x is dimensionless, Δ needs to have units of energy, and thus must be multiplied by ℏ. On the other hand, J_z has units of ℏ. Therefore B needs to have units of frequency, and thus the right hand side of the corresponding expression in Eq. (3) must be divided by an ℏ. Other formulas in this article can be handled in a similar manner.

B. The four dimensional squeezing Hamiltonian

The generation of spin squeezing requires the presence of a nonlinearity, represented to lowest order by a term quadratic in one of the spin operators in the relevant Hamiltonian [18]. However, Eq. (2) is linear in each of the spin operators. It may not be readily obvious that the
coupled dynamics of the two spins can lead to squeezing, and it would assist our intuition if $H_M$ could be reduced, even if in some restricted regime, to the form of a spin squeezing Hamiltonian familiar from the literature. In order to effect such a reduction, we proceed by identifying a regime in which the pseudospin 1/2 can be eliminated adiabatically. As we show below, this results in an effective spin-squeezing Hamiltonian for the spin 3/2 degree of freedom. A similar procedure has been used earlier in the case of nuclear spin squeezing; in that case however the eliminated spin is real [60]. The derivation begins with the Heisenberg equations implied by Eq. (2) for the system variables

\begin{align*}
\dot{\sigma}_x &= 2\theta \sigma_y, \\
\dot{\sigma}_y &= -2\theta \sigma_x - 2\tilde{E}\sigma_z (J_z \cos \theta - J_x \sin \theta), \\
\dot{\sigma}_z &= 2\tilde{E}\sigma_y (J_z \cos \theta - J_x \sin \theta), \\
J_x &= \tilde{B} J_y - \tilde{E} \theta \sigma_y J_z, \\
J_y &= -\tilde{B} J_x + \tilde{E} \sigma_x (J_z \cos \theta + J_x \sin \theta), \\
J_z &= -\tilde{E} \sin \theta \sigma_z J_y.
\end{align*}

We now consider the regime

$$\tilde{\Delta} > \tilde{E}, \tilde{B},$$

(10)

e.g. such that the Lambda-doublet splitting is larger than the Stark as well as Zeeman shifts. In our calculations below we will work with $\tilde{E}/\tilde{\Delta} \simeq 0.25$, which corresponds to an electric field of 100 V/cm, the lower bound stipulated by the value of stray fields currently affecting experiments [74]. We will also consider $\tilde{B}/\tilde{\Delta} \lesssim 0.1$, corresponding to a magnetic field of 20 G, which can easily be achieved experimentally.

In the regime indicated by Eq. (10), $\sigma_x$ and $\sigma_y$ will vary at the high rate $\sim 2\tilde{\Delta}$ and may be thought of as the ‘fast’ variables of our problem. We will see below that with this assumption $\sigma_z$ ceases to be a dynamical variable, i.e. takes on a constant value. On the other hand, $J_x$, $J_y$, and $J_z$, varying at the low rates $\sim \tilde{B}$ and $\sim \tilde{E}$ (to first order), may be thought of as the ‘slow’ variables of the problem. We now adiabatically eliminate the fast spin variables $\sigma_x$ and $\sigma_y$ in Eqs. (4)-(5) by setting the time derivatives in those equations equal to zero. The resulting solutions are

\begin{align*}
\sigma_x &= -\frac{\tilde{E} C}{\tilde{\Delta}} (J_z \cos \theta - J_x \sin \theta), \\
\sigma_y &= 0, \\
\sigma_z &= C,
\end{align*}

(11)-(13)

where we have retained $C$ for generality. Note that the adiabatic solution $\sigma_y = 0$ forces $\sigma_z$ to be a constant [see Eq. (6)], as mentioned above. We now use the solutions of Eqs. (11)-(13) to adiabatically eliminate the fast spin 1/2 degrees of freedom from Eq. (2). Dropping a constant term proportional to $\tilde{\Delta}$, we obtain the adiabatic Hamiltonian for the spin 3/2 variables

$$H_a = -\tilde{B} J_z - \frac{C\tilde{E}^2}{\tilde{\Delta}} (J_z \cos \theta - J_x \sin \theta)^2,$$

(14)

which clearly contains terms nonlinear in the angular momentum components, and can therefore enforce squeezing.

Below, we will show that some standard squeezing Hamiltonians can be recovered from Eq. (14), and also explore the squeezing effects of this Hamiltonian for arbitrary $\tilde{B}, \tilde{E}$ and $\theta$, within the limits prescribed by the validity of the effective Hamiltonian [Eq. (2)]. Subsequently, we will compare these results with numerical calculations based on the full eight-dimensional Hamiltonian of Eq. (2), which accounts for non-adiabatic effects and thus allows us to examine the validity of the adiabatic elimination process used in arriving at Eq. (14). We note that Eq. (11) does not stipulate any relationship between $\tilde{E}$ and $\tilde{B}$, other than that they both have to be smaller than $\tilde{\Delta}$. We will use this flexibility below to adjust the field magnitudes to optimize squeezing.

III. SPIN SQUEEZING DYNAMICS

A. Spin squeezing using the four-dimensional adiabatic Hamiltonian $H_a$

In this section we consider spin squeezing using the four-dimensional adiabatic Hamiltonian of Eq. (14). We provide analytic and numerical results, as appropriate.

1. One-axis twisting

For $\tilde{B} = 0, \theta = 0, C = 1$, Eq. (14) gives the Kitagawa-Ueda Hamiltonian [18],

$$H_{KU} = \tilde{\kappa} J_z^2,$$

(15)

where

$$\tilde{\kappa} = -\frac{\tilde{E}^2}{\tilde{\Delta}}.$$  

(16)

The theoretical analysis for spin squeezing using $H_{KU}$ was first provided by Kitagawa and Ueda [18], and more recently by Rochester et al. [65]. Nonetheless, we restate the procedure here, in order to compare with fully numerical calculations to be presented later. The recipe for
the analysis goes as follows. Using the four-dimensional matrix for the \( J = 3/2 \) operator \( J_z \), we write the matrix form for \( H_{\text{KU}} \). We then obtain the time evolution operator

\[
U_{\text{KU}} = e^{-iH_{\text{KU}}t},
\]

which is also a four-dimensional matrix. We can then obtain the time evolution of any observable \( \mathcal{O} \) by using the relation \( \mathcal{O}(t) = U_{\text{KU}}^{-1} \mathcal{O} U_{\text{KU}} \). In this way we find the matrix forms of the observables \( J_x(t) \) and \( J_y(t) \). In order to find the most suitable axis for spin squeezing, it is convenient to consider a further rotation by an angle \( \eta \) about the \( x \) axis [18], i.e.

\[
J_{y,n}(t) = e^{inJ_z(t)} J_y(t) e^{-inJ_z(t)},
\]

and so on for other observables. The operators \( J_z(t) \) and \( J_x(t) \) are unaffected by this rotation, of course.

For our initial state, we choose, following Kitagawa and Ueda, the (coherent) stretched state along the \( x \) axis [18],

\[
|\psi\rangle_{\text{KU}} = |J = \frac{3}{2}, M = \frac{3}{2}, \hat{x}\rangle = 2^{-3/2} \sum_{k=0}^{3} \left( \begin{array}{c} 3 \\ k \end{array} \right) \frac{3}{2} \frac{3}{2} - k \langle k \rangle,
\]

which we have expanded in the \( z \) basis on the right hand side. We note that the current level of control over the OH ground state manifold should readily allow this state to be prepared [22]. Using the initial state \( |\psi\rangle_{\text{KU}} \) we find the expectation values \( \langle J_{y,n}(t) \rangle, \langle J_{y,n}(t) \rangle \), etc., and hence the variances such as

\[
(\Delta J_{y,n}(t))^2 = \langle J_{y,n}^2(t) \rangle - \langle J_{y,n}(t) \rangle^2.
\]

This procedure yields the relevant quantities [65]

\[
\langle J_x(t) \rangle = \frac{3}{2} \cos^2 \hat{\kappa} t,
\]

\[
(\Delta J_{y,n}(t))^2 = \frac{3}{4} \left[ 1 + \frac{M}{2} + \frac{\sqrt{M^2 + N^2}}{2} \cos (2n + \delta) \right],
\]

\[
(\Delta J_{z,n}(t))^2 = \frac{3}{4} \left[ 1 + \frac{M}{2} - \frac{\sqrt{M^2 + N^2}}{2} \cos (2n + \delta) \right]
\]

where

\[
M = 1 - \cos 2\hat{\kappa} t, \quad N = 2 \sin 2\hat{\kappa} t, \quad \delta = \frac{1}{2} \tan^{-1} \left( \frac{N}{M} \right).
\]

As pointed out earlier [18, 65], the \( y \) quadrature is maximally squeezed for \( \cos (2n_{\text{opt}} + \delta) = -1 \), i.e. along the axis

\[
n_{\text{opt}} = \frac{\pi}{2} - \delta,
\]

in the \( y - z \) plane. The amount of squeezing is quantified by the parameter introduced by Wineland et al. [20]

\[
\xi_{y,n} = \sqrt{3} \frac{\langle (\Delta J_{y,n}(t)) \rangle}{|\langle J_x(t) \rangle|},
\]

and, analogously,

\[
\xi_{z,n} = \sqrt{3} \frac{\langle (\Delta J_{z,n}(t)) \rangle}{|\langle J_x(t) \rangle|}.
\]

Squeezing occurs when either \( \xi_{y,n} \) or \( \xi_{z,n} \) is less than one. We have shown a plot of \( \xi_{y,n_{\text{opt}}} \) in Fig. 2. The blue (solid) line is the analytical prediction of Eq. (25) and shows that the \( y \) quadrature is squeezed periodically. As found by Rochester et al. [65], for \( J = 3/2 \) the minimum value of the squeezing parameter is \( m \xi_{y,n_{\text{opt}}} \approx 0.75 \), consistent with Fig. 2. The red (dashed) curve in Fig. 2 corresponds to a numerical calculation of squeezing using the full effective Hamiltonian of Eq. (2), which incorporates the effects of nonadiabaticity, see Section III B below. As can be seen, nonadiabatic effects change the magnitude and periodicity of the squeezing.

![FIG. 2:](Color online) Plot of \( \xi_{y,n_{\text{opt}}} \) as a function of the dimensionless time \( \hat{t} \) where \( \hat{\kappa} \) is defined in Eq. (16). The parameters are \( \Delta = 1.66 \) GHz, \( E = 100 \) V/cm and \( B = 0 \), implying \( \hat{\kappa} = 48 \) MHz. Squeezing occurs when \( \xi_{y,n_{\text{opt}}} < 1 \). The blue (solid) curve is the analytical prediction from Eqs. (24) and (25) based on the adiabatic approximation of Eq. (10), with \( E/\Delta \approx 0.25 \). The red (dashed) curve is the numerical calculation using the eight dimensional effective Hamiltonian of Eq. (2). As can be seen, nonadiabatic effects significantly change the magnitude and periodicity of the squeezing.
the case where matrices of dimension 5 or lower. Some results for the calculation, which can be found in closed form only since the eigenvalues of the Hamiltonian are required for stretched state along the direction.

In this section we consider spin squeezing in the presence of a magnetic field. For $B \neq 0$, and $\theta = \pi/2$, Eq. (14) takes the form

$$H_{LNL} = -\tilde{B} J_z + \tilde{\kappa} J_z^2.$$  

(27)

This Hamiltonian is, to within a unitary anti-clockwise rotation of $\pi/2$ around the $y$ axis, the same as proposed earlier by Law, Ng and Leung [30, 78–80]. These authors suggested adding the uniform field term to the Kitagawa-Ueda Hamiltonian as it yielded greater squeezing for longer times. Analytic solutions to the spin squeezing dynamics of Eq. (27) are not available for arbitrary spin $J$. Generally, analytic results can be found only for $J \leq 2$, since the eigenvalues of the Hamiltonian are required for the calculation, which can be found in closed form only for matrices of dimension 5 or lower. Some results for the case where $J = 3/2$ is a collective spin have been published in the literature [80, 81]. We provide additional expressions in order to discuss the details of our problem.

To determine the squeezing, we follow a procedure similar to that of Section 3.1 but consider the initial stretched state along the $z$ direction

$$|\hat{i}\rangle_{LNL} = |0, 0, 0, 1\rangle,$$  

(28)

and determine the squeezing about the $x$ and $y$ axes. We find

$$\langle J_x(t) \rangle = \langle J_y(t) \rangle = 0,$$  

(29)

$$\langle J_z(t) \rangle = \frac{3}{2} \left[ 1 - \left( \frac{\tilde{\kappa}}{P} \sin Pt \right)^2 \right],$$  

(30)

$$\langle (\Delta J_x(t))^2 \rangle = \frac{3}{4} \left[ 1 + 2\tilde{\kappa} \tilde{B} \left( \sin Pt \right)^2 \right],$$  

(31)

$$\langle (\Delta J_y(t))^2 \rangle = \frac{3}{4} \left[ 1 - 2\tilde{\kappa} \left( \tilde{B} - \tilde{\kappa} \right) \left( \frac{\sin Pt}{P} \right)^2 \right],$$  

(32)

where

$$P = \sqrt{B^2 - 2\tilde{B}\tilde{\kappa} + \tilde{\kappa}^2}.$$  

(33)

Using Eqs. (29), we can find the squeezing parameters

$$\xi_x = \sqrt{3} \frac{\langle (\Delta J_x(t))^2 \rangle}{\langle J_x(t) \rangle},$$  

(34)

and

$$\xi_y = \sqrt{3} \frac{\langle (\Delta J_y(t))^2 \rangle}{\langle J_y(t) \rangle},$$  

(35)

Plots of the squeezing dynamics are shown in Fig. 4a) for the same parameters as in Fig. 2 but with $\tilde{B} = 20$ G. The dashed curves represent the analytical results for $\xi_x$ [Eqs. (34)] (blue) and $\xi_y$ [Eq. (35)] (red). The solid curves are the corresponding numerical calculations using $H_M$ from Eq. (2). It can be seen from the numerically calculated red (solid) curves in Fig. 4a) that the Law-Ng-Leung approach is quite robust to nonadiabatic effects. In Fig. 4 we have chosen a magnetic field optimized using the following procedure. From the analytic result of Eq. (35), it can be seen that at multiples of the time $t_S$

$$t_S = \frac{\pi}{4P},$$  

(36)

the squeezing parameter for the $y$ quadrature attains an extremum value given by

$$\xi_y(t = t_S) = \frac{2\sqrt{(r^2 - r + 1)(r^2 - 2r + 2)}}{2r^2 - 2r + 1},$$  

(37)

where the dimensionless ratio

$$r = \frac{\tilde{B}}{|\tilde{\kappa}|}.$$  

(38)

The denominator of $\xi_y(t = t_S)$ vanishes only for the complex values $r = (1 \pm i)/2$, which are excluded by experiment. Thus, $\xi_y^{\text{min}}$ stays finite as $r$ varies, as can be seen.
FIG. 4: (Color online) Plots of $\xi_{x,y}$ as functions of the dimensionless time $P t$ where $P$ is defined in Eq. (33). The parameters are $\Delta = 1.66$ GHz, $E = 100$ V/cm, $B = 20$ G, implying $P = 144$ MHz and (a) $\theta = 90^\circ$ (b) $\theta = 85^\circ$ (c) $\theta = 80^\circ$ (d) $\theta = 75^\circ$. Squeezing occurs when $\xi_{x,y} < 1$. The dashed curves are the analytical predictions for $\xi_x$ [Eq. (34)] (blue) and $\xi_y$ [Eq. (35)] (red). The solid curves represent numerical calculations carried out using the eight dimensional effective Hamiltonian of Eq. (2). As can be seen by comparing with Fig. 2, the squeezing is quite robust to nonadiabatic effects. Also, deviations of about $5^\circ$ away from the nominal value of $90^\circ$ for field alignment do not affect the squeezing greatly.

from Fig. 5 Differentiation of Eq. (37) readily yields a minimum value $\xi^\text{min}_y(t = t_S) \simeq 0.8$, which occurs at $r \simeq 3.3$, indicated by the vertical line in Fig. 5. This optimized value of $r$ corresponds to the magnetic field 20 G used in Fig. 4(a). For simplicity, unlike in Ref. [80], we have not found the time-dependent axis of optimum squeezing, which can lead to even better squeezing than we have presented.

3. General case

In this section we consider spin squeezing as a function of the angle between the electric and magnetic fields. The interest in this degree of freedom arises from the necessity of accounting for possible misalignments between the electric and magnetic fields in the laboratory, e.g. away from the nominal value of $\theta = \pi/2$ for $H_{LNL}$, see Section IIA.2 While this case can be solved analytically as well, the expressions are lengthy and we provide numerical solutions instead. The Hamiltonian is

$$H_g = -\tilde{B} J_z + \tilde{\kappa} (J_z \cos \theta - J_x \sin \theta)^2.$$  (39)

Before we proceed further, we mention that this Hamiltonian, when rotated anti-clockwise by an angle $\theta$ about the $y$ axis yields

$$H_g' = e^{i\theta J_y} H_g e^{-i\theta J_y} = -\tilde{B} (J_z \cos \theta - J_x \sin \theta) + \tilde{\kappa} J_x^2,$$  (40)

which is of the form considered earlier by Agarwal and Puri for arbitrary $J$ [21].

Numerical plots are presented in Fig. 4 for (b) $\theta = 85^\circ$ (c) $\theta = 80^\circ$ and (d) $\theta = 75^\circ$, respectively. The dashed curves are the numerical implications of Eq. (39) for $\xi_x$ [Eq. (34)] (blue) and $\xi_y$ [Eq. (35)] (red). The solid curves are the corresponding numerical calculations starting from Eq. (2). As can be seen, the squeezing is quite robust to field misalignment. Only at about $\theta = 75^\circ$ does the pattern change noticeably from that at $\theta = 90^\circ$. Interestingly, while misalignment degrades squeezing in
the y quadrature, it does not correspondingly introduce squeezing in the x quadrature.

B. Spin squeezing using the eight-dimensional effective Hamiltonian $H_M$

In this section we describe our spin squeezing calculations using the full eight-dimensional Hamiltonian $H_M$ of Eq. (2). This enables us to quantitatively examine the adiabatic approximation made in deriving the four-dimensional spin squeezing Hamiltonian $H_a$ of Eq. (14). The calculation proceeds as follows. We begin with the eight-dimensional matrix representation of $H_M$ from Eq. (48). Although the treatment can be carried out analytically, the expressions are very long, and we calculate instead numerically the time evolution operator

$$U_M = e^{-iH_M t},$$

which is also an eight-dimensional matrix. Starting from the initial state $|\psi(0)\rangle$, represented by an eight-dimensional column matrix, the state vector $|\psi(t)\rangle$ at any later time $t$ is

$$|\psi(t)\rangle = U_M |\psi(0)\rangle.$$

The density matrix of the full system can then be easily found

$$\rho(t) = |\psi(t)\rangle \langle \psi(t)|.$$

The reduced density matrix of the spin 3/2 system can then be found by tracing over the spin 1/2 degrees of freedom, i.e.

$$\rho_{3/2}(t) = \text{Tr}_{1/2} [\rho(t)].$$

From here the expectation values of the relevant operators can be calculated, such as

$$\langle J_x(t) \rangle = \text{Tr}_{3/2} [J_x \rho_{3/2}(t)],$$

and therefore also the squeezing parameters, as for example in Eq. (34). It may be useful to mention that for Section III A 1 the initial state is now written as

$$|i\rangle_{KU} = \frac{1}{2\sqrt{2}} (0, 0, 0, 0, 1, \sqrt{3}, \sqrt{3}, 1),$$

and for Sections III A 2 and III A 3 as

$$|i\rangle_{LNL} = (0, 0, 0, 0, 0, 0, 0, 1).$$

Comparison of the four and eight-dimensional results can be seen in Figs. 2-4 and has been described in the preceding sections. These plots imply that while non-adiabatic effects can be important, the adiabatic approximation captures the basic spin dynamics reasonably well, and the intuition afforded by this approximation about the existence of squeezing is well founded. Better agreement can be produced by assuming a smaller adiabaticity parameter, but currently this is limited by stray electric fields in the experiments. The key point is that even in the presence of non-adiabaticity, squeezing exists.

IV. DETECTION OF SPIN SQUEEZING

The proposed spin squeezing may be detected by performing quantum tomography on the OH ground state manifold, which would yield the density matrix, from which squeezing information can readily be extracted. Such procedures can be carried out for OH in analogy to experiments performed earlier on atomic [63] and nuclear [64] systems. In the laboratory, the predicted squeezing will be degraded by damping and noise, due to molecular collisions and trap loss. In the present work, we have justifiably neglected these effects, since they occur at typical rates of Hz (collisions) [3, 4, 9] or KHz (trap loss) [7], while squeezing is generated at frequencies of MHz [Fig. 4].

V. CONCLUSION

We have proposed a scheme for spin squeezing the ultracold OH molecule, in the context of ongoing experiments. Production of such nonclassical states is expected to be useful for spectroscopy, magnetometry and stereochemistry. We have identified an accessible parameter regime where single-axis twisting as well as uniform field squeezing can be implemented with the use of static fields only. Since we do not propose to use optical or microwave
fields, our scheme is free from damping and decoherence due to spontaneous emission and optical pumping. In our analysis, we have shown how to optimize the field values and also investigated the effect of field misalignment on the squeezing. To our knowledge, our work is the first concrete proposal for spin squeezing single noninteracting molecules with angular momentum greater than $1/2$. We note that with the use of additional electric and magnetic fields, other spin squeezing Hamiltonians may also be realized using OH, such as the one proposed by Raghavan et al. [31]. Also, a more accurate description of the OH ground state can be reached by including more states in the Hamiltonian, accounting for fine and hyperfine structure and electric quadrupole interactions and magnetic fields, other spin squeezing Hamiltonians can also be extended to the ground states of other polar paramagnetic molecules such as $^2\Sigma_{1/2}$ LiO and $^3\Phi_2$ CeO.

We would like to thank S. Marin for useful discussions.

VI. APPENDIX

In this Appendix we provide, for the reader’s convenience, the matrix representation of $H_M$ from Eq. (48).

$H_M =$

$$
\begin{pmatrix}
-\frac{\hbar}{2} - \frac{\mu_B}{2} B & 0 & 0 & 0 & \frac{\mu_e}{2} E \cos \theta & \frac{\mu_e}{2} E \sin \theta & 0 & 0 \\
0 & -\frac{\hbar}{2} - \frac{\mu_B}{2} B & 0 & 0 & -\frac{\mu_e}{2} E \cos \theta & -\frac{\mu_e}{2} E \sin \theta & 0 & 0 \\
0 & 0 & -\frac{\hbar}{2} + \frac{\mu_B}{2} B & 0 & \frac{\mu_e}{2} E \cos \theta & \frac{\mu_e}{2} E \sin \theta & 0 & 0 \\
0 & 0 & 0 & -\frac{\hbar}{2} + \frac{\mu_B}{2} B & \frac{\mu_e}{2} E \cos \theta & -\frac{\mu_e}{2} E \sin \theta & 0 & 0 \\
-\frac{\hbar}{2} \mu_e E \cos \theta & -\frac{\hbar}{2} \mu_e E \sin \theta & 0 & 0 & \frac{\mu_e}{2} E \cos \theta & -\frac{\mu_e}{2} E \sin \theta & 0 & 0 \\
-\frac{\hbar}{2} \mu_e E \sin \theta & -\frac{\hbar}{2} \mu_e E \cos \theta & 0 & 0 & -\frac{\mu_e}{2} E \cos \theta & \frac{\mu_e}{2} E \sin \theta & 0 & 0 \\
0 & -\frac{\hbar}{2} \mu_e E \sin \theta & -\frac{\hbar}{2} \mu_e E \cos \theta & -\frac{\hbar}{2} \mu_e E \cos \theta & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{\hbar}{2} \mu_e E \sin \theta & -\frac{\hbar}{2} \mu_e E \cos \theta & 0 & 0 & 0 & 0
\end{pmatrix}
$$

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