Ultracold heteronuclear molecules and ferroelectric superfluids

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We analyze the possibility of a ferroelectric transition in heteronuclear molecules consisting of Bose-Bose, Bose-Fermi or Fermi-Fermi atom pairs. This transition is characterized by the appearance of a spontaneous electric polarization below a critical temperature. We discuss the existence of a ferroelectric Fermi liquid phase for Fermi molecules and the existence of a ferroelectric superfluid phase for Bose molecules characterized by the coexistence of ferroelectric and superfluid orders. Lastly, we propose an experiment to detect ferroelectric correlations through the observation of coherent dipole radiation pulses during time of flight.

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Arguably one of the next frontiers in ultracold atomic and molecular physics is the study of two-species atomic mixtures \( 1 \ 2 \ 3 \ 4 \ 5 \ 6 \), and ultracold heteronuclear molecules composed of two-species alkali atoms such as KRb \( 7 \ 8 \ 9 \), RbCs \( 10 \) and NaCs \( 11 \). This frontier may be advanced through the use of Feshbach resonances which have already been observed in mixtures of two-species alkali atoms \( 12 \ 13 \ 14 \), and may also become a crucial tool for tuning physical properties of heteronuclear systems.

Ultracold heteronuclear molecules made of Bose-Bose, Bose-Fermi or Fermi-Fermi atom pairs offer many new opportunities compared to standard (Bose or Fermi) atomic systems because of their additional degrees of freedom. For instance, when heteronuclear diatomic molecules are formed from neutral atoms, electric charge is transferred from one atom to the other leading to an electric dipole moment \( |P| = Q|d|d \), where \( d \) is the separation and \( Q(d) \) is the effective charge transfer between constituent atoms \( 13 \). These electric dipoles have equal magnitudes but random orientations at high temperatures leading to a vanishing average electric polarization. However, at low temperatures, the dipoles may all point to a particular direction producing a finite average electric polarization density \( \langle P \rangle \), characteristic of a ferroelectric state. In addition, when ultracold heteronuclear molecules form a Bose-Einstein condensate (BEC) a ferroelectric superfluid state proposed in this manuscript may be accessible experimentally.

Our main results are as follows. When heteronuclear molecules are composite fermions (Bose-Fermi pairs), a phase transition occurs separating a paraelectric Bose liquid (PBL) from a ferroelectric Fermi liquid (FFL), as shown in Fig. \( 1 \)a. These phases do not exist in standard condensed matter systems, since all experimentally known ferroelectrics are very good insulators \( 16 \), and are not Fermi liquids. Furthermore, when heteronuclear molecules are composite bosons (Bose-Bose or Fermi-Fermi pairs), a ferroelectric transition with critical temperature \( T_{FE} \) may occur either above or below the BEC temperature \( T_{BEC} \). When the molecular dipole moment and/or density are sufficiently large then \( T_{FE} > T_{BEC} \) leading to a paraelectric Bose liquid (PBL) for \( T > T_{FE} \), a ferroelectric Bose liquid (FBL) for \( T_{FE} > T > T_{BEC} \), and to a ferroelectric BEC (FBEC) for \( T < T_{BEC} \), as shown in Fig. \( 1 \)b. When the molecular dipole moment and/or density are sufficiently low then \( T_{FE} < T_{BEC} \) leading to a paraelectric Bose liquid (PBL) for \( T > T_{BEC} \), a paraelectric BEC for \( T_{BEC} > T > T_{FE} \), and to a ferroelectric BEC (FBEC) for \( T < T_{FE} \), as shown in Fig. \( 1 \)c. The FBEC phase corresponds to a ferroelectric superfluid.

Hamiltonian: To describe all these phases of ultracold heteronuclear molecules, we use the Hamiltonian density

\[
H(r) = \sum_{\sigma} \psi_{\sigma}^* (r) \left[ -\frac{\nabla^2}{2M} - \mu + V(r) \right] \psi_{\sigma} (r) + \frac{1}{2} \sum_{\sigma,\sigma'} \int d\mathbf{r}' n_{\sigma'}(\mathbf{r}) U_{\sigma}(\mathbf{r},\mathbf{r}') n_{\sigma}(\mathbf{r}) - \frac{1}{2} \sum_{\alpha,\beta} \int d\mathbf{r}' P_{\alpha}(\mathbf{r}') J_{\alpha,\beta}(\mathbf{r},\mathbf{r}') P_{\beta}(\mathbf{r}),
\]

describing a weakly interacting gas of dilute po-
lar molecules, where ψ^α_σ(r) creates a Bose (Fermi) molecule at position r with pseudo-spin-σ, and n_α(r) = ψ^α_σ*(r)ψ_σ(r) is the density operator. The first term in Eq. (1) is the kinetic energy, where μ is the chemical potential, and V(r) is the trapping potential. The second term is the density-density interaction between Bose (Fermi) molecules, and for a contact interaction is given by U_d(r, r') = Uδ(Δr), where U = 4πα/M is the amplitude of the interaction and δ(Δr) is the delta function with Δr = r - r'. Here, α is the scattering length of the corresponding Bose (Fermi) molecules, and M is the molecular mass. The third term is the electric dipole-dipole interaction between molecular dipoles at positions r and r', where P(r) = p(r) ∑_σ n_σ(r) is the polarization operator, and p(r) is the molecular dipole moment at position r. The electric dipole-dipole interaction is given by J(r, r') = ∑_α,β p_α(r)J_α,β(r, r')p_β(r'), where

J_α,β(r, r') = \frac{1}{4π\varepsilon_0} \frac{3|\Delta r_α\Delta r_β|/|\Delta r|^2 - \delta_α,\beta}{|\Delta r|^3}. \hspace{1cm} (2)

Here, δ_α,β is the Kronecker-delta and {α, β} = {1, 2, 3} label the vector components.

**Electric polarization:** Within the Hartree-Fock approximation, the Hamiltonian density reduces to

\[ H_0(r) = -\nabla^2 \frac{2M}{\hat{m}} - \hat{\mu} + V(r) + UN_0(r) \]

- \sum_{\alpha,\beta} \int dr' p_\alpha(r)J_{\alpha,\beta}(r, r')p_\beta(r'), \hspace{1cm} (3)

where the electric polarization density P_0(r) = p(r)n_0(r), with n_0(r) = ∑_σ n_0_σ(r) being the local density of Bose (Fermi) molecules at r. The spatially averaged polarization \( <P> = \int dr P_0(r)/V_c \) can be rewritten as

\[ <P> = \frac{1}{V_c} \int dr p(r) \sum_{i,\sigma} |\phi_i(r)|^2 f_\eta(\epsilon_i), \hspace{1cm} (4) \]

where V_c is the sample volume, ϕ_i(r) and ε_i are eigenfunctions and eigenvalues of the Hamiltonian H_0(r), and f_\eta(ε) = 1/[e^{βε} - 1] is the Bose (Fermi) distribution for Bose (Fermi) molecules when η = 1 (-1). The solution of Eq. (4) is non-trivial, however analytical insight can be gained for homogeneous systems where V(r) = 0 and P_0(r) = P_0 is independent of r. We discuss the homogeneous case first and then analyze the case of a harmonic trap.

**Ferroelectric critical temperature:** In the ferroelectric state, all molecular dipoles are pointing along the same direction \( \hat{m} \) such that p(r) = p|p|\hat{m} and P_0 = |P_0|\hat{m}. The critical temperature T_{FE} for the ferroelectric transition is found from the slope of Eq. (4) with respect to P_0 evaluated at P_0 = 0, leading to

\[ 1 + \bar{J}(q \rightarrow 0) \left( \frac{\partial N}{\partial \mu} \right)_T = 0, \hspace{1cm} (5) \]

from which T_{FE} can be calculated. Here, \( \bar{J}(q) \) with q = k - k' is the Fourier transform of J(Δr), and N is the number of Bose or Fermi molecules. Introducing the Kac parameter γ as a cutoff for short distances (|Δr| < 1/γ) leads to \( \bar{J}(q) = \sum_{\alpha,\beta} p_\alpha \bar{J}_{\alpha,\beta}(k,k')p_\beta \), where

\[ \bar{J}_{\alpha,\beta}(k,k') = \frac{S(\bar{q})}{\varepsilon_0} \left( \frac{3q_\alpha q_\beta}{|q|^2} - \delta_{\alpha,\beta} \right). \hspace{1cm} (6) \]

Here, \( S(\bar{q}) = \sin(\bar{q}/\bar{q}^3) - \cos(\bar{q}/\bar{q}^2) \) where \( \bar{q} = |q|/\gamma \). Thus, we obtain an implicit relation for the T_{FE}

\[ 1 - 2|p|^2 3\kappa(T_{FE}) = 0, \hspace{1cm} (7) \]

in terms of the molecular density \( n = N/V_c \) and the isothermal compressibility \( \kappa(T) = (1/n^2)(\partial n/\partial \mu)_T \).

The ferroelectric instability is accompanied by a divergence of the dielectric function in the long-wavelength and low-frequency limit. Using linear response theory, the dielectric function \( ε(q, i\omega_n) \) can be related to the density-density correlation function \( C(q, τ) = \langle T_r n(q, τ)n(-q, 0) \rangle \) and to \( \bar{J}(q) \) via

\[ \frac{1}{\varepsilon(q, i\omega_n)} = 1 - \frac{\bar{J}(q)}{V_c} \int_0^{1/T} dτ e^{i\omega_n τ} C(q, τ), \hspace{1cm} (8) \]

where \( n(q, τ) \) is the density operator. In the long-wavelength and low-frequency limit, C(q, τ) is directly related to \( \kappa(T) \) via the compressibility sum rule [17]. Therefore, a divergent dielectric function occurs when \( ε(q \rightarrow 0, i\omega_n \rightarrow 0) = 0 \) leading to \( 1 + \bar{J}(q \rightarrow 0) \partial N/\partial \mu)_T = 0 \), which is identical to Eq. (4). This relation can be applied to both Bose and Fermi systems. Next, we discuss T_{FE} for a weakly interacting (a ≪ λ) and dilute (na^3 ≪ 1) gas of Bose and Fermi molecules, where a is the scattering and λ is the thermal length.

**Fermi molecules:** As a first application of Eq. (4), we analyze T_{FE} for a weakly interacting gas of Fermi molecules at any T. In this case, the molecular density is given by \( n = 2F_{3/2}(z)[1 - 2F_{1/2}(z)a/λ_F]/λ^2_F \) where \( λ_F = [2π/(MT)]^{1/2} \) is the thermal length, and leading to \( \kappa(T) \approx F_{1/2}(z)/F_{3/2}(z) - 2F_{-1/2}(z)a/λ_F/(nT) \) where \( 0 ≤ z = \exp(β\mu) ≤ \infty \) is the fugacity, and \( F_{3/2}(z) = 1/[Γ(ν)] \int_0^{∞} x^{ν-1} dx/[z^{-1}e^x + 1] \) is the Fermi integral. Here, Γ(ν) is the Gamma function. Thus, we obtain

\[ T_{FE} = \frac{2|p|^2}{3\varepsilon_0} \left[ \frac{F_{1/2}(z_c)}{F_{3/2}(z_c)} - \frac{2a}{λ^2_F}F_{-1/2}(z_c) \right] n, \hspace{1cm} (9) \]

where \( z_c = \exp(μ/T_{FE}) \). Notice that, in the classical (z_c ≪ 1) limit, Eq. (4) reduces to \( T_{FE} = 2|p|^2(1 - 2z_a/λ^2_F)n/(3ε_0) \), which shows that T_{FE} ∝ n for a gas of classical electric dipoles. The T_{FE} for an ideal (non-interacting) gas of Fermi molecules can be obtained by setting a = 0. For an ideal gas, when T_{FE}
is much smaller than the Fermi energy $\epsilon_F$, we obtain $T_{FE} \approx (2\sqrt{3}/\pi e_F|p|^2 n/(\epsilon_0 e_F) - 1)^{-1/2}$, which is valid for $|p|^2 n/(\epsilon_0 e_F) > 1$ and $|p|^2 n/(\epsilon_0 e_F) - 1)^{-1/2} \ll 1$. For $T > T_{FE}$ a PFL phase exists and for $T < T_{FE}$ a FFL phase appears as shown in Fig. 2(a).

**Bose molecules for $T \geq T_{BEC}$:** As a second application of Eq. 4, we analyze for a weakly interacting gas of Bose molecules when $T \geq T_{BEC}$. In this case, the molecular density is given by $n = B_{3/2}(z)/\lambda_B^3 + n_s$, where $n_s = z/[V_c(1-z)] = \alpha(T)n$ is the density of bosons in the condensed (zero-energy) state. Here, $\alpha(T) = 1 - (T/T_{BEC})^{3/2}$ where $T_{BEC} = 2\pi[n/\zeta(3/2)]^{2/3} / M$ is the critical BEC temperature for non-interacting dilute bosons, and $\zeta(x)$ is the Zeta function. In this case, $\kappa(T) = [B_{1/2}/(z)]^{1/2} V_n n_s^2 / (n^2 T)$, which diverges in the thermodynamic limit $\zeta(3)$ when $\{N, V_c\} \to \infty$ but $n = N/V_c$ is a constant. Thus, we obtain

$$T_{FE} = 2|p|^2/3 \xi_0 \left[ B_{1/2}(z_c) / B_{3/2}(z_c) \right] (n - n_s) + V_n n_s^2 / z_c ,$$

which is always smaller than $T_{BEC}$, and reduces to the non-interacting limit of Eq. 13 in the absence of BEC.

The two cases of Bose molecules allows the construction of the phase diagrams indicated in Fig. 2(b) and 2(c), respectively, where the PBL, FBL, PBEC and FBEC are identified depending on the existence of a spontaneous average electric polarization $\langle P \rangle$ and/or of a BEC fraction $\langle \phi \rangle$. The ferroelectric superfluid phases proposed here may be experimentally observed with currently available cooling techniques only when $T_{FE}$ is large enough. This requirement imposes a condition on the size of the electric dipole moments of the molecules, and it is discussed next for the Fermi-Fermi Bose molecules.

**Fermi-Fermi Bose molecules:** To set the scale, we consider the specific example of Li-K molecules consisting of $^6$Li and $^{40}$K atoms in their ground state, where $|p| = 3.6$ Debye $\Gamma^3$. We also choose an equal population mixture of $^6$Li and $^{40}$K atoms with parameters $N = 10^5$ and $V = 10^{-7}$ cm$^3$ leading to $T_{BEC} \approx 0.099\xi_F$ and $T_{FE} \approx 21\xi_T$. However, for a molecule with $|p| = 1.0$ Debye, $T_{FE} \approx 1.67\xi_T$. Here, $\xi_F = k_F^2/(2m_F)$ is the Fermi energy, where $m_F$ is half of the reduced mass of Li and K atoms, and $k_F$ is the Fermi momentum with $n = k_F^3/(6\pi^2)$.

**For the two-species Fermi-Fermi mixtures (such as $^6$Li and $^{40}$K), we propose a schematic phase diagram of temperature $T$ versus scattering parameter $1/(k_F\xi_F)$ for an equal mixture of two-species Fermi-Fermi mixtures.**

**Heteronuclear molecules in a trap:** The trapping potential of polar molecules is given by $V(r) = -\alpha|E(r)|^2 - |p| \cdot E(r)$, which are due to the coupling of the laser electric field $E(r)$ with the induced and permanent dipole moments $p_{ind} = \alpha E(r)$ and $p_{per} = p$, respectively. We assume that $E(r) = E_0 \exp[-r^2/(2w^2) - \gamma^2/(2w_0^2)]$ has a gaussian profile controlled by the widths $w_r$ and $w_z$, where $r^2 = x^2 + y^2$. Thus, the trapping potential can be approximated by $V(r) = V_0 + M\Omega_p^2 \rho^2/2 + M\Omega_z^2 z^2/2$, where

$$\Omega_p^2 = \frac{2}{\beta \mu_p}$$

and

$$\Omega_z^2 = \frac{2}{\beta \mu_z}$$

are the magnetic dipole moments of the molecule.
where $V_0 = -\alpha E_0^2 - |\mathbf{p}|E_0 \cos \theta$, and $\Omega_i = (2\alpha E_0 + |\mathbf{p}|E_0 \cos \theta)/(Mw_0^2)$ are the characteristic frequencies of the harmonic trap along $i = \rho, z$ directions. Here, $\theta$ is the angle between $\mathbf{p}$ and $\mathbf{E}(\mathbf{r})$. When $w_z \gg w_\rho$ ($w_z \ll w_\rho$) the trap is cigar (disc) shaped.

In the ground state of the system, the Thomas-Fermi approximation can be applied leading to

$$U n_0(\mathbf{r}) = \tilde{\mu} - V(\mathbf{r}) + \int d\mathbf{r}' J(\mathbf{r}, \mathbf{r}') n_0(\mathbf{r}')$$ (12)

and the electric polarization density is given by $\mathbf{P}(\mathbf{r}) = \rho n_0(\mathbf{r})$. The integral equation can be solved analytically when $\beta = [|\mathbf{p}|^2/(4\pi\varepsilon_0 V_c)]/U \ll 1$, corresponding to a small ratio between the characteristic electric dipolar energy $|\mathbf{p}|^2/(4\pi\varepsilon_0 V_c)$ and the characteristic contact interaction energy $U/V_c$. To zeroth order in $\beta$, the electric polarization is $\mathbf{P}(\mathbf{r}) = \mathbf{P}_{TF}(\mathbf{r}) = \rho n_{TF}(\mathbf{r})$, where

$$n_{TF}(\mathbf{r}) = n_{\text{max}} \left[ 1 - \rho^2 / \rho_0^2 - z^2 / z_0^2 \right].$$ (13)

Here, $n_{\text{max}} = (\tilde{\mu} - V_0)/U$, $\rho_0^2 = (\tilde{\mu} - V_0)/(M\Omega_0^2)$ and $z_0^2 = (\tilde{\mu} - V_0)/(M\Omega_c^2)$. The correction to first order in $\beta$ for the cigar shaped trap is

$$\delta \mathbf{P}(\mathbf{r}) = \beta \frac{4\pi}{18} \tilde{n} \rho_0^2 \left[ c_1 - c_2 (\rho^2 / \rho_0^2 - z^2 / z_0^2) \right],$$ (14)

where $c_1$ and $c_2$ are numerical coefficients, and $\tilde{n} = N/V_c$ is the average molecular density. Since $\mathbf{E}(\mathbf{r})$ is much stronger than the local electric fields produced by electric dipolar interactions, the net polarization $\mathbf{P}(\mathbf{r}) = \mathbf{P}_{TF}(\mathbf{r}) + \delta \mathbf{P}(\mathbf{r})$ points along $\mathbf{E}(\mathbf{r})$.

![FIG. 3. Direction of the polarization vector during time of flight for a ferroelectric state, when the external electric field is a) perpendicular, and b) parallel to the easy axis of polarization. The clouds in each frame are not drawn to scale.](image)

To distinguish between the fully polarized paraelectric state and the true ferroelectric superfluid, we propose two experiments, as shown schematically in Fig. 3, where $\mathbf{E}(\mathbf{r})$ is turned off between times I and II. In case (a), the external electric field and the easy axis for polarization are perpendicular. For the ferroelectric state, the polarization flips between times I and II (within nanoseconds to microseconds) towards the axial direction which corresponds to the easy axis for the electric polarization. This flip produces a short pulse of coherent dipolar radiation proportional to $N^2$. However, for the fully polarized paraelectric state the polarization relaxes and reduces to zero within microseconds, producing a longer pulse of incoherent dipolar radiation proportional to $N$. A second coherent pulse may occur in time of flight for the ferroelectric state as the anisotropy inversion in the cloud expansion takes place between times III and IV, and causes a second flip of the electric polarization towards the new easy axis. In case (b), the external electric field and the easy axis for polarization coincide. For the ferroelectric state, the polarization remains along the easy axis between times I and II, and between times III and IV when the anisotropy inversion occurs, the polarization flips towards the new easy axis with emission of coherent dipolar radiation (proportional to $N^2$). In this case only one pulse (within nanoseconds to microseconds) should be observed after a few milliseconds of expansion. For the paraelectric state similar results as in case (a) apply.

In conclusion, we analyzed the possibility of a ferroelectric transition in Bose-Bose, Bose-Fermi or Fermi-Fermi heteronuclear molecules. This transition is characterized by the appearance of a spontaneous electric polarization below a critical temperature where the dielectric function diverges. We obtained the order parameter equation, evaluated the transition temperature and the electric polarization for ultracold heteronuclear (Bose or Fermi) molecules. We discussed the existence of a ferroelectric Fermi liquid phase for polar Fermi molecules, and the existence of a ferroelectric superfluid phase for polar Bose molecules characterized by the coexistence of ferroelectric and superfluid orders. We also proposed an experiment to detect ferroelectric correlations via the observation of coherent dipole radiation pulses during time of flight. We thank NSF (DMR-0304380) for support.

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