Effective-mass model and magneto-optical properties in hybrid perovskites

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Hybrid inorganic-organic perovskites have proven to be a revolutionary material for low-cost photovoltaic applications. They also exhibit many other interesting properties, including giant Rashba splitting, large-radius Wannier excitons, and novel magneto-optical effects. Understanding these properties as well as the detailed mechanism of photovoltaics requires a reliable and accessible electronic structure, on which models of transport, excitonic, and magneto-optical properties can be efficiently developed. Here we construct an effective-mass model for the hybrid perovskites based on the group theory, experiment, and first-principles calculations. Using this model, we relate the Rashba splitting with the inversion-asymmetry parameter in the tetragonal perovskites, evaluate anisotropic g-factors for both conduction and valence bands, and elucidate the magnetic-field effect on photoluminescence and its dependence on the intensity of photoexcitation. The diamagnetic effect of exciton is calculated for an arbitrarily strong magnetic field. The pronounced excitonic peak emerged at intermediate magnetic fields in cyclotron resonance is assigned to the $3D_{\pm 2}$ states, whose splitting can be used to estimate the difference in the effective masses of electron and hole.

Hybrid organic-inorganic perovskites such as CH$_3$NH$_3$PbI$_3$ represents a revolutionary breakthrough for low-cost solar cells because of their desirable optical and carrier transport properties. The materials also exhibit many intriguing features, including strong spin-orbit coupling and the associated Rashba effect, large-radius Wannier excitons, and novel magnetic-field effect (MFE) in photoluminescence (PL) and photoconduction, and show promise in light-emitting and thermoelectric applications.

These outstanding properties are interconnected and are ultimately determined by the material’s unusual electronic structure, which has been intensively studied by a variety of density-functional calculations. While such first-principles calculations are indispensable in predicting the crystal structure, carrier effective mass, and band gap, they become increasingly unwieldy in studying processes involving excited states and under external fields. An alternative is to develop an effective-mass Hamiltonian, which is both tractable and transparent in physics with parameters determined by experimentally measured properties. These properties, such as effective masses and g-factors, are usually obtained from magneto-optical studies, which turn out to be a major experimental means of validating the principle of the band theory of semiconductors.

Exciton, an electron-hole pair bounded by the Coulomb interaction, is a fundamental excitation in semiconductors. The exciton binding energy in the hybrid perovskites is critical to photovoltaic and light-emitting efficiencies and has been a subject of intense debate. This controversy can be resolved via a definitive measurement of magneto-optical absorption (cyclotron resonance), which reveals characters of exciton as well as constituent electron and hole. To take advantage of the wealth of information, a detailed analysis of cyclotron resonance is needed. While diamagnetic response of an exciton is similar to that of a hydrogen, a key difference is that the electron and hole in an exciton have a comparable effective mass, particularly in the hybrid perovskites.

A moderate magnetic field less than 1 T is found to be able to influence exciton PL in CH$_3$NH$_3$PbI$_3$, indicating that magnetic field is a versatile tool for studying excitons and free carriers. This MFE has been attributed to the $\Delta g$ (the difference between electron and hole g-factors) mechanism, frequently encountered in organic radical pairs. However, the lack of knowledge on the g-factors in CH$_3$NH$_3$PbI$_3$ hampers the development of a clear understanding of the MFE. In addition, the MFE is sensitive to the intensity of photoexcitation, which is not well understood.
Here we construct an effective-mass model of CH₃NH₃PbI₃ based on information available in literature. This model, which can be extended to other hybrid perovskites by using suitable parameters, reveals connections among the g-factors, effective masses, and Rashba spin splittings. Using this model, we examine the MFE on exciton PL and find that the MFE is controlled by the interplay of exchange energy, exciton (spin) relaxation time, and the Zeeman energy. Besides the Δg mechanism, a Σg (summation of the electron and hole g-factors) mechanism can manifest itself in the MFE. The dependence of MFE on the intensity of photoexcitations is quantitatively explained in terms of the screening effect by the photogenerated carriers, which greatly reduces the exchange coupling of excitons. The diamagnetic effect on excitons under an arbitrarily large magnetic field is reliably calculated in an excellent agreement with recent cyclotron measurements. The experimentally observed pronounced excitonic absorption peak, induced by the magnetic-field, can be attributed to the 3D D⊥ states, whose energy splitting can be used to determine the difference in electron and hole effective masses. Our results demonstrate the efficacy of the effective-mass model in understanding magneto-optical properties and suggest it a foundation for systematically studying many other transport, optical, and spintronic processes in the hybrid perovskites.

Results
Model. Crystalline CH₃NH₃PbI₃ can have the high-temperature α1-phase with the pseudo cubic (O₃) symmetry, the intermediate-temperature β-phase with the tetragonal (C₄ᵥ) symmetry, and the low-temperature orthorhombic γ phase. Phase transitions from high to low temperatures, being of group-subgroup type, take place at 333 K and 150 K, respectively25,26. We focus in this paper on the β-phase, which is also a good description of the approximately uniaxial γ-phase25. In the β-phase, PbI₆ octahedra are misalign with the C-axis (symmetry axis of C₄ᵥ), and the structure is noncentrosymmetric.

First-principles calculations indicate that the valence and conduction bands are mainly associated with cationic (Pb) s and p orbitals, respectively15–17,27, denoted as S, X, Y, and Z. The direct band gap is located at R point17, which has the same C₄ᵥ symmetry as the crystal structure. Since physically relevant states are those close to the band extrema, we derive band structure in the neighborhood of R point, via the k·p method, where k is the wave vector away from the R point. In this method, the wave function at k is expressed as ψₖ = eⁱʳ·σ(r) with uₖ(r) being the basis function of n'th band at R point. We note that the k·p Hamiltonian for zinc-blende semiconductors is not suitable for the tetragonal perovskites15. In the absence of magnetic field, the Hamiltonian can be written as $H = H₀ + H_{SO}$, where $H₀ = m^* / 2 M + V(r)$ is spin-independent part and $H_{SO} = \hbar^2 / 2 m \nabla \times \mathbf{p} \cdot \sigma$ is the spin-orbit coupling (SOC). Here V(r) is periodic potential, p is momentum, m is free electron mass, c is the speed of light, and $\sigma$ are the Pauli matrices.

In the β-phase, the potential should be an identical representation of group C₄ᵥ, a subgroup of the cubic group O₃, and therefore can be expressed in terms of the O₃ representations, in particular, its first three irreducible representations, $\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3$. Neglecting the trivial $\Gamma_1$ representation, we write $V(r) = \sum \epsilon_i d_i$, where $d_i = 2 z^2 - x^2 - y^2$ and $d_2 = x^2 - y^2$ are the basis functions of $\Gamma_2$, and $d_1 = x$, $d_2 = y$, and $d_3 = z$ are the basis functions of $\Gamma_3$. By requiring $D(G) \langle \mathbf{r} \rangle = \langle \mathbf{r} \rangle$ with G being the symmetry operators in C₄ᵥ, $c_2 = c_3 = c_1 = 0$. The nonzero $c_1$ reflects a crystal-field splitting between Z and X (Y), $(X|H₀|X) = (Y|H₀|Y) = -(Z|H₀|Z)/2 = \delta/3$. And $c_1$ originates from the lack of inversion asymmetry in C₄ᵥ, giving rise to $\langle S|H₀|Z \rangle = \langle Z|H₀|S \rangle = c_1 \langle S|z|Z \rangle \equiv \epsilon$.

The Hamiltonian $H₀$ up to the second order of $k$, can be written as19,20

$$H₀ = \frac{\hbar^2 k^2}{2m} + \begin{pmatrix} E_s + iP_x k_x & iP_y k_y & iP_z k_z & iP_x k_y + \epsilon & iP_y k_z + \epsilon & iP_z k_x + \epsilon \\ -iP_x k_y & N k_y k_y & M k_y^2 + M k_z^2 + \frac{\delta}{3} & N k_y k_y & N k_y k_y & N k_y k_y \\ -iP_y k_z & M k_z^2 + M k_z^2 + \frac{\delta}{3} & N k_z k_z & M k_z^2 + k_y^2 & L k_z^2 - \frac{2\delta}{3} \\ -iP_z k_x + \epsilon & N k_z k_z & N k_z k_z & M k_z^2 + k_y^2 & L k_z^2 - \frac{2\delta}{3} \end{pmatrix}$$

(1)

Here $E_s$ is the valence-band maximum, $L_o$, $M_o$, and $N_o$ are parameters due to the interaction between the conduction bands with far bands other than the valence band, and $P_1 = \frac{\hbar^2}{m} \langle S \rangle - i \langle \nabla |Z \rangle$ and $P_2 = \frac{\hbar^2}{m} \langle S \rangle - i \langle \nabla |X \rangle$ are the Kane parameters that connect the valence-band and conduction-band orbitals20. The SOC among the p orbitals mixes up and down spins, $\lambda = i(X|H₀|Y) = i(Y|H₀|Z) = i(Z|H₀|X)$, which is particularly strong in the hybrid perovskites due to the heavy element Pb, $\lambda = 1.2–1.5$ eV•Å, and cannot be treated as a perturbation.

The crux of the k·p method is that the basis functions of $uₖ(r)$ should be the eigenstates of $H$ at $k = 0$20, which can be achieved by choosing the following basis functions $uₖ(r)$.

$$v_{\alpha}(r) = S \uparrow \langle \alpha \rangle,$$

$$c_{\alpha}(r) = \frac{\cos \xi}{\sqrt{2}} [X + (-)iY] \uparrow \langle \alpha \rangle - \sin \xi |Z \rangle \uparrow \langle \alpha \rangle,$$

$$c'_{\alpha}(r) = -\frac{1}{\sqrt{2}} [X + (-)iY] \uparrow \langle \alpha \rangle.$$
\[ c''_{\pm} = \mp \sin \frac{\xi}{2} \left[ (X - \mp iY) \uparrow \downarrow + \cos \xi Z \downarrow \uparrow \right], \]  

(5)

with \( \tan 2\xi = \frac{2 \sqrt{2} \lambda}{\lambda^2 - \delta^2} \). The angular momentum is \( s = 1/2 \) for the valence band \( v \pm \), and \( j = 1/2 \) (or \( l = s \)) for the first conduction band \( c \pm \). The two upper conduction bands, \( c_{\pm} ' \) and \( c_{\pm} '' \), have \( j = 3/2 \), with \( j_z = \pm \frac{3}{2} \) for \( c_{\pm} ' \) and \( j_z = \pm \frac{1}{2} \) for \( c_{\pm} '' \). The diagonal elements at \( k = 0 \) in these basis functions are

\[ E_v, E_c = -2.8 \text{ eV}, -1.2 \text{ eV}, 0.6 \text{ eV}, \]  

which fix the parameter values, \( \lambda = 1.4 \text{ eV}, \delta = -0.7 \text{ eV}, \) and \( \sin \xi = 0.411 \).

Figure 1. Schematic diagram of band edges and their angular momenta in CH₃NH₃PbI₃. The optical absorption spectrum is adapted from ref. 29.
Here $E_{a}(k)$ is the energy of $m$th band, which, for small $k$, can be approximated by the band-edge value. Taking into account the non-commutative relations among $k$ components, we obtain the effective Hamiltonians, up to the second order of $k$, for the valence and conduction bands, with basis functions of $\nu_{z}$ and $\epsilon_{z}$ in Eqs (2) and (3),

\[
\widehat{H}_{v}(k) = \widehat{E}_{v} - \frac{\hbar k^{2}}{2m_{0\perp}} - \frac{\hbar k^{2}}{2m_{\parallel}} + \alpha_{v}(k_{y}\sigma_{x} - k_{x}\sigma_{y}) + \frac{\mu_{B}}{2} (g_{v} \sigma_{x} B_{z} + g_{h_{z}}(\sigma_{x} B_{x} + \sigma_{y} B_{y})),
\]

\[
\widehat{H}_{c}(k) = \widehat{E}_{c} + \frac{\hbar k^{2}}{2m_{0\perp}} + \frac{\hbar k^{2}}{2m_{\parallel}} + \alpha_{c}(k_{y}\sigma_{x} - k_{x}\sigma_{y}) + \frac{\mu_{B}}{2} (g_{v} \sigma_{x} B_{z} + g_{h_{z}}(\sigma_{x} B_{x} + \sigma_{y} B_{y})),
\]

where $\mu_{B} \equiv e\hbar/(2mc)$ is the Bohr magneton, $\widehat{E}_{v} \equiv E_{v} + \zeta^{2} \cos^{2} \xi(\zeta_{v} - E_{c}) + \zeta^{2} \sin^{2} \xi(\zeta_{v} - E_{c})$ and $\widehat{E}_{c} \equiv E_{c} + \zeta^{2} \sin^{2} \xi(\zeta_{v} - E_{c})$, which can be approximated by $E_{v}$ and $E_{c}$.

The effective masses of valence band along and perpendicular to the C-axis in Eq. (9) are expressed as

\[
-\frac{1}{m_{0\parallel}} = \frac{1}{m} + \frac{2P_{\parallel}^{2}}{\hbar^{2}} \frac{\cos^{2} \xi}{E_{v} - E_{c}} + \frac{\sin^{2} \xi}{E_{v} - E_{c}},
\]

\[
-\frac{1}{m_{\perp}} = \frac{1}{m} + \frac{2P_{\perp}^{2}}{\hbar^{2}} \left( \frac{1}{2} \frac{\sin^{2} \xi}{E_{v} - E_{c}} + \frac{\cos^{2} \xi}{E_{v} - E_{c}} \right) + \frac{1}{E_{v} - E_{c}}.
\]

It is interesting to note that $m_{0\parallel}$ ($m_{\perp}$) depends on the interaction with the conduction bands via the Kane parameter $P_{\parallel}$ ($P_{\perp}$). Similarly, the effective masses of the conduction band along and perpendicular to the C-axis are

\[
\frac{1}{m_{0\parallel}} = \frac{1}{m} + \frac{2P_{\parallel}^{2}}{\hbar^{2}} \left( L_{2} \sin^{2} \xi + M_{2} \cos^{2} \xi \right) + \frac{2P_{\parallel}^{2}}{\hbar^{2}} \frac{\sin^{2} \xi}{E_{v} - E_{c}},
\]

\[
\frac{1}{m_{\perp}} = \frac{1}{m} + \frac{2P_{\perp}^{2}}{\hbar^{2}} \left( \frac{L_{1} + M_{1}}{2} \cos^{2} \xi + M_{2} \sin^{2} \xi \right) + \frac{2P_{\parallel}^{2}}{\hbar^{2}} \frac{\cos^{2} \xi}{E_{v} - E_{c}},
\]

which are influenced by the interaction with the valence band, as well as by the symmetric parameters $L_{1}$ and $M_{1}$, stemming from the interaction with far bands. The anisotropic effective masses for the valence and conduction bands have been extensively calculated by several first-principles approaches$^{16,17}$. One of the most accurate values are given in ref. 17, which are also consistent with recent cyclotron resonance measurements$^{23}$, $m_{0\parallel} = 0.21 m$, $m_{0\perp} = 0.23 m$, $m_{\parallel} = 0.15 m$, and $m_{\perp} = 0.21 m$. From these effective masses, we obtain the Kane parameters, $P_{\parallel} = 7.64 eV \AA$ and $P_{\perp} = 6.95 eV \AA$, as well as the symmetric parameters $mL_{1}/\hbar^{2} = -25.90$ and $mM_{1}/\hbar^{2} = 23.39$.

A free electron possesses a magnetic moment of its spin and has a $g$-factor of $g_{0} = 2.0023$. The SOC enables the electron orbital motion to contribute to the magnetic moment and, consequently, the effective $g$-factor deviates from $g_{0}$. In Eq. (9), the $g$-factors of the valence-band edge along and perpendicular to the C-axis are

\[
g_{h\parallel} = g_{0} + 2mP_{\parallel} \left( \frac{\cos^{2} \xi}{E_{v} - E_{c}} + \frac{\sin^{2} \xi}{E_{v} - E_{c}} - \frac{1}{E_{v}} \right),
\]

\[
g_{h\perp} = g_{0} + 2m\sqrt{\xi} \sin \xi \cos \xi P_{\parallel} \left( \frac{1}{E_{v} - E_{c}} - \frac{1}{E_{v} - E_{c}} \right).
\]

We see that the $g$-factors depend on the energies of conduction-band edges as well as the Kane parameters. In contrast to the effective mass, $g_{h\parallel}$ is connected to the conduction bands only via $P_{\perp}$. This is understandable because a magnetic field $B$ affects the electron orbital motion perpendicular to the field. For the same reason, $g_{h\perp}$ is connected to the conduction bands via both $P_{\parallel}$ and $P_{\perp}$. Using the values of $P_{\parallel}$ and $P_{\perp}$, we obtain the $g_{h\parallel} = -0.472$ and $g_{h\perp} = -0.354$, which are similar to the value in 2H-PbI$_{2}$, $g_{0} = -0.432$. The negative $g$-factor means that the up spin has a lower energy than the down spin.

The conduction-band $g$-factors along and perpendicular to the C-axis are

\[
g_{c\parallel} = 2[ - (3k_{1} + 2) \cos^{2} \xi + \sin^{2} \xi ] + 2mP_{\parallel} \frac{\cos^{2} \xi}{E_{v} - E_{c}},
\]

\[
g_{c\perp} = 2[ - (3k_{2} + 1) \sqrt{\xi} \sin \xi \cos \xi - \sin^{2} \xi ] + \frac{2\sqrt{\xi} mP_{\perp} \sin \xi \cos \xi}{E_{v} - E_{c}},
\]

which depend on the antisymmetric Luttinger parameters $k_{1}$ and $k_{2}$, in addition to the $P_{\parallel}$ and $P_{\perp}$. Thus the values of $g_{h\parallel}$ and $g_{h\perp}$ can be used to determine $k_{1}$ and $k_{2}$. Experimentally, the excited $g$-factor are measured from the energy splitting between left- and right-circularly polarized absorption$^{33,34}$ and PL$^{11}$, which, as we will discuss below, is
**Figure 2. g-factors and cyclotron masses of conduction and valence bands.** Left panels describe the electron ($g_e$) and hole ($g_h$) g-factors as a function of angle $\theta$ between the C-axis and the applied magnetic field. Right panels describe the electron ($m_{ce}$) and hole ($m_{ch}$) cyclotron masses.

If we use $g_{\|} + g_{\perp} |\epsilon| = 1.2$, as in ref. 33, we find $g_{\|} = 1.672$ and $\kappa_1 = 0.269$. If we further assume $\kappa_2 = \kappa_4$, we have $g_{\perp} = 2.281$. These values are also similar to those of electrons in 2H-PbI$_2$, $g_{\|} = 1.4$ and $g_{\perp} = 2.43$.2.

Since both the g-factors and the effective masses are anisotropic, the effective spin splitting and the cyclotron frequency depend on the angle $\theta$ between the magnetic field and the C-axis,

$$g_{\perp}(\theta) = \left( \frac{g_{\perp}(\theta)}{g_{\perp}(\theta)} + \frac{g_{\perp}(\theta)}{g_{\perp}(\theta)} \right)^{1/2}, \quad m_{\perp}(\theta) = \frac{eB}{m_{\perp}(\theta) \sin^2 \theta}. \quad (15)$$

The derivations can be found in the Methods section. We plot in Fig. 2 the g-factors and the effective cyclotron mass, $m_{\perp}(\theta)$ as a function of angle $\theta$. At $\theta = 0$, $g_{\perp}(\theta) = g_{\perp}(\theta)$ and $m_{\perp}(\theta) = m_{\perp}(\theta)$. At $\theta = \pi/2$, $g_{\perp}(\theta) = g_{\perp}(\theta)$ and $m_{\perp}(\theta) = m_{\perp}(\theta)$.

**Rashba splitting.** The Rashba term, $E_{\text{Rashba}}(k) = \alpha_{\text{Rashba}}(k, \sigma_x - k, \sigma_y)$ in Eqs (9) and (10), destroys the spin degeneracy, giving rise to energy-momentum dispersion, $E_{\text{Rashba}}(k) = \frac{\hbar k^2}{2m_\perp} + \frac{\hbar^2 k_z^2}{2m_\perp} \pm \mid \alpha_{\text{Rashba}} \mid k_z$ for the conduction band and $E_{\text{Rashba}}(k) = \frac{\hbar k^2}{2m_\perp} - \frac{\hbar^2 k_z^2}{2m_\perp} \pm \mid \alpha_{\text{Rashba}} \mid k_z$ for the valence band, as plotted in Fig. 3.

The Rashba strengths $\alpha_{\text{Rashba}}$ are directly related to the $C_p$ potential $\zeta$-parameter that characterizes the inversion asymmetry of the structure,

$$\alpha_{\text{Rashba}} = \sqrt{2} \zeta \cos \zeta \sin \zeta \left( \frac{1}{E_v - E_c} - \frac{1}{E_c - E_v} \right) P_{\perp}, \quad (16)$$

$$\alpha_{\text{Rashba}} = \sqrt{2} \zeta \cos \zeta \sin \zeta \left( \frac{1}{E_v - E_c} - \frac{1}{E_c - E_v} \right), \quad (17)$$

which indicate that the Rashba splittings in the valence and conduction bands are correlated. Currently the Rashba splittings obtained from different first-principles calculations vary significantly and direct measurements, such as spin-polarized photoemission and spin-flip Raman scattering, of CH$_3$NH$_3$PbI$_3$ are not yet available. For $\zeta = 0.5$ eV, we have $\alpha_{\text{Rashba}} = 0.565$ and $\alpha_{\text{Rashba}} = 1.088$ eVÅ.

**Exciton wavefunctions.** Hybrid perovskite CH$_3$NH$_3$PbI$_3$ has a large dielectric constant $\varepsilon$, and the excitons are of the Wannier type, whose wave functions can be written as35

$$\psi_{\text{exc}}(r) = \sum_{j_{\epsilon,\chi}} \Phi_{j_{\epsilon,\chi}}(r) \Psi_{j_{\epsilon,\chi}}(r)$$

where $j_{\epsilon,\chi} = \pm$, $\pm = \pm \hat{r} v_{\chi}$, with $\hat{r}$ being the time-reversal operator. $\Phi_{j_{\epsilon,\chi}}(r) - r_j$ is the envelope function describing the relative motion of electron and hole and may have $S$, $P$, or $D$ characteristics in low magnetic fields, which gradually transforms to that of Landau wave functions with increase of magnetic field.
The hole (electron) state $\mathbf{v}_j$ follows the $\Gamma^+_6$ ($\Gamma^-_6$) representation of $C_4v$. With $\Phi^{rr}_{\mathbf{r}_e - \mathbf{r}_h}$ being the 1S state, the exciton wavefunctions can be characterized by the $C_4v$ representations, $\Gamma \otimes \Gamma = \Gamma \oplus \Gamma \oplus \Gamma^+ \oplus \Gamma^-$.

$$
\begin{align*}
\psi_1 &= \frac{1}{\sqrt{2}}(c_v \mathbf{v}_e - c_e \mathbf{v}_h) = -\frac{1}{2} \cos \xi (X + iY) S \downarrow \downarrow_h + \frac{1}{2} \cos \xi (X - iY) S \uparrow \uparrow_h - \frac{1}{2} \sin \xi \uparrow \downarrow_h + \frac{1}{2} \sin \xi \downarrow \uparrow_h,
\psi_2 &= \frac{1}{\sqrt{2}}(c_v \mathbf{v}_e + c_e \mathbf{v}_h) = -\frac{1}{2} \cos \xi (X + iY) S \downarrow \downarrow_h - \frac{1}{2} \cos \xi (X - iY) S \uparrow \uparrow_h + \frac{1}{2} \sin \xi \uparrow \downarrow_h - \frac{1}{2} \sin \xi \downarrow \uparrow_h,
\psi^+_5 &= c_v \mathbf{v}_e = -\frac{1}{\sqrt{2}} \cos \xi (X + iY) S \downarrow \downarrow_h - \sin \xi \uparrow \downarrow_h - \sin \xi \downarrow \uparrow_h,
\psi^-_5 &= c_v \mathbf{v}_h = -\frac{1}{\sqrt{2}} \cos \xi (X - iY) S \uparrow \uparrow_h + \sin \xi \downarrow \uparrow_h - \sin \xi \downarrow \uparrow_h.
\end{align*}
$$

The total angular momentum $J = j_e + j_h$ is $J = 0$ for $\psi_1$, $(J, J_z) = (1, 0)$ for $\psi_2$, and $(J, J_z) = (1, \pm 1)$ for $\psi^\pm_5$. The absorption and emission of these states are proportional to the modular square of their electric-dipole elements,

$$
\langle \psi_i | e \cdot p | 0 \rangle = 0, \quad \langle \psi_2 | e \cdot p | 0 \rangle = i \sqrt{2} \sin \xi c_e P_\|, \quad \langle \psi^+_5 | e \cdot p | 0 \rangle = -i \cos \xi c_e P_\perp, \quad \langle \psi^-_5 | e \cdot p | 0 \rangle = i \cos \xi c_e P_\perp
$$

with $c_e = \frac{1}{\sqrt{2}}(c_e \pm i c_h)$.

The above selection rules in the hybrid perovskites is in stark contrast to those in $\pi$-conjugated organic materials with weak SOCs, where the electron (hole) has zero angular momentum ($l_z = 0$ for $\pi$ orbitals) and $J = 0$ is dipole forbidden whereas $J = 1$ is dipole allowed. As we will see below, this difference gives rise to a far richer physics of MFE in the hybrid perovskites.

**Paramagnetic effects on excitons.** The four 1S exciton states, $\psi_1, \psi_2$, and $\psi^\pm_5$, in general, are not degenerate in energy because of possible exchange interaction between spins $H_{ex} = \frac{1}{2} \sum (\sigma^e_\alpha \sigma^h_\beta + \sigma^e_\beta \sigma^h_\alpha)$, where $\sigma^e/2 = j_e$ and $\sigma^h/2 = j_h$. Consequently the energies of these excitons $E_1 = -J - 2J_\perp, \quad E_2 = -J_\perp + 2J_\perp, \quad E_3 = J_\parallel$.

An applied magnetic field can modify the exciton energy via the Zeeman energy,

$$
H = H_{ex} + H_Z = H_{ex} + \frac{1}{2} \mu_B[g_{\|} \sigma^e_\| B_\| + g_{\perp} \sigma^e_\perp B_\perp + \sigma^h_\| B_\| + g_{\perp} \sigma^h_\perp B_\perp + g_{\|} (\sigma^e_\| B_\| + \sigma^h_\| B_\|)].
$$

Figure 3. Rashba effect in the conduction and valence bands near the $R$ point. Left (right) panel is for $k$ along the $[0, 1, 1]$ ($[0, 1, 1]$) direction. $\zeta = 0.5$ eV.
It should be noted that from the time reversal symmetry, the hole's $g$-factor, including the sign, is identical to that of the valence electron. Since we are concerned with relatively weak magnetic field, we temporarily neglect the diamagnetic effect, which is proportional to $B^2$ and shift states equally in energy.

In the Faraday configuration with $B$ along the C-axis, $B = (0, 0, B)$, $\psi_i^\pm$ will split in energy, $E_{\psi_i^\pm, \psi_i}$ = $J_1 + \frac{1}{2}(g_1 + g_{\text{hh}})\mu_B B$, and the splitting in absorption and luminescence peaks of left- and right-circularly polarized light, would be $(g_1 + g_{\text{hh}})\mu_B B$. The magnetic field $B$ will also mix $\psi_1$ and $\psi_2$, with

$$H_1 = \begin{pmatrix} E_1 & (g_1 - g_{\text{hh}})\mu_B B/2 \\ (g_1 - g_{\text{hh}})\mu_B B/2 & E_2 \end{pmatrix},$$

and the energy of eigenstates become $E_{\psi_1^\pm, \psi_2}(B) = J_1 + \frac{1}{2}(g_1 \pm g_{\text{hh}})\mu_B B + (g_1 - g_{\text{hh}})^2\mu_B^2 B^2$ and their wave functions are $\tilde{\psi}_i = b_1\psi_1 + b_2\psi_2$. Hence, with increase of the magnetic field, $\tilde{\psi}_i$ will gain oscillator strength, $|\langle \tilde{\psi}_i | c, p_2 \rangle|_i^2 \propto |b_1|^2$, and flare up, while $\tilde{\psi}_i$ will lose oscillator strength, $|\langle \tilde{\psi}_i | c, p_2 \rangle|_i^2 \propto |b_2|^2$, as illustrated in Fig. 4.

In the Vogt configuration with $B$ perpendicular to the C-axis, $B = (B, 0, 0)$, we can construct transverse and longitudinal states out of $\psi_{5L}^\pm$ states, $\psi_{5T} = \frac{1}{2\sqrt{2}}(c_+ \varphi_+ + c_- \varphi_-)$ and $\psi_{5L} = \frac{1}{\sqrt{2}}(c_+ \varphi_+ - c_- \varphi_-)$, which have polarization along the y and x axis, respectively. It is readily to verify that in this configuration, pair ($\psi_1, \psi_{5L}$) as well as pair ($\psi_2, \psi_{5T}$) are coupled via the magnetic field, with

$$H_2 = \begin{pmatrix} E_1 & (g_{\text{hh}} - g_{\text{hh}})\mu_B B/2 \\ (g_{\text{hh}} - g_{\text{hh}})\mu_B B/2 & E_5 \end{pmatrix},$$

and their energies are $E_{\psi_1, \psi_{5L}}(B) = J_1 + \frac{1}{2}(g_{\text{hh}} + g_{\text{hh}})\mu_B B + (g_{\text{hh}} - g_{\text{hh}})^2\mu_B^2 B^2$ and $E_{\psi_2, \psi_{5T}}(B) = J_{\perp} \pm \frac{1}{2}(g_{\text{hh}} - g_{\text{hh}})\mu_B B + (g_{\text{hh}} + g_{\text{hh}})^2\mu_B^2 B^2$. Figure 4 also plots the exciton energies $E_1, E_2, E_{\psi_{5L}}$, and $E_{\psi_{5T}}$, as well as their corresponding oscillator strengths $|\langle \psi_1 | p_2 \rangle|^2$ as a function of the magnetic field.

**Magnetic-field effect on photoluminescence.** The PL intensity in CH$_3$NH$_3$PbI$_3$ is found to be susceptible to a magnetic field at low temperatures. In the Faraday configuration, the magnetic field couples $\psi_1$ and $\psi_2$ excitons. Since only the recombination of $\psi_1$ can give rise to luminescence, the magnetic-field-induced change in

![Figure 4](image-url)
populations of $\psi_2$ and $\psi_1$ would lead to an MFE. We employ the Bloch equation of the density matrix to systematically describe the population dynamics,

$$\frac{\partial \hat{\rho}}{\partial t} = \frac{i}{\hbar} \left[ \rho, H \right] + \left( \frac{\partial \hat{\rho}}{\partial t} \right)_g - \hat{\rho},$$ (23)

where $\hat{\rho}$ is a $2 \times 2$ density matrix spanned by $\psi_1$ and $\psi_2 = \sum_{m,n} \rho_{mn} |\psi_m\rangle \langle \psi_n|$, $|\psi_m\rangle$ with $m, n = 1, 2$, $(\partial \rho/\partial t)_g$ represents the generation of the exciton states, which is finite only for diagonal terms, $(\partial \rho_{nn}/\partial t)_g = F_g \rho_{nn}$, because the PL in the MFET measurements is not resonantly excited. $\tau$ is the relaxation time of these exciton states, which includes both recombination $\tau_1^{-1}$ and spin relaxation $\tau_2^{-1}, \tau_2^{-1} = \tau_1^{-1} + \tau_2^{-1}, \tau_2^{-1} > 10^{-6} \gg \tau_1^{-1} \approx 10^{-10} \Delta \xi_{11}$. In the steady state, $\partial \rho/\partial t = 0$, the densities at $\psi_1$ and $\psi_2$ can be written as $\rho_{11} = i \Delta \rho_{21} = -i \Delta \rho_{12} = \rho_{22} = i \Delta \rho_{21}[F_1 - F_2](1 + (\Delta g \mu_B B^2 + 16 \Delta_1^2 \rho_{11}^2)/\tau_1^2]$.

The intensity change in PL is due to the change in $\rho_{22}$,

$$\Delta I_1 \propto \frac{(\Delta g \mu_B B^2 \tau^2)}{1 + (\Delta g \mu_B B^2 + 16 \Delta_1^2 \rho_{11}^2)/\tau_1^2}.$$ (24)

When the exchange is significant with $4 f_1 < \tau \gg 1, \Delta I_1 \propto B^2/(1 + (B/\Delta g \mu_B B^2))$ with $B = 4 f_1 / \Delta g \mu_B B$. In this regime, the MFE is suppressed because the magnetic field cannot overcome the exchange to effectively alter the populations on the exciton states for $H < 1T$.

Using the Bloch equation, we express the PL change in the $\psi_1$ and $\psi_{32}$ manifold as

$$\Delta I_2 \propto \frac{(\Delta g \mu_B B^2 \tau^2)}{1 + (\Delta g \mu_B B^2 + 4 \Delta_1 \rho_{11}^2)/\tau_1^2},$$ (25)

where $\Delta g_{11} = g_{c,1} - g_{h,1}$, and the PL change in the manifold of $\psi_2$ and $\psi_{3T}$ as

$$\Delta I_3 \propto \frac{(\Sigma g \mu_B B^2 \tau^2)}{1 + (\Sigma g \mu_B B^2 + 4 \Delta_1 \rho_{11}^2)/\tau_1^2},$$ (26)

where $\Sigma g_{11} = g_{c,1} + g_{h,1}$. The MFE in the $\psi_1$ and $\psi_{32}$ manifold, $\Delta I_2$, depends on the difference in the $g$-factors along the $x$-axis, the direction of the magnetic field, in a very similar fashion as $\Delta I_1$.

The MFE in the $\psi_1$ and $\psi_{32}$ manifold, $\Delta I_2$, however, depends on the summation of the electron and hole $g$-factors along the $x$-axis. Thus in addition to the $\Delta g$ mechanism, a $\Sigma g$ mechanism is taking effect in the hybrid perovskites. In the former, the magnetic field modulates the populations between states $J = 0$ and $(J, J_m) = (1, 0)$, which can be visualized as the electron and hole spins precess along the magnetic field in the opposite directions. In the latter, the magnetic field modulates populations between $(J, J_m) = (1, 0)$ and $(1, \pm 1)$, which can be visualized as the electron and hole spins precess along a transverse magnetic field in the same direction. The $\Sigma g$ mechanism is particularly important if the exchange is approximately isotropic, $f_1 \approx f_3$, where the $J = 1$ triplet states are degenerate in energy, and according Eq. (26), $\Delta I_3$ is then completely determined by the exciton relaxation time $\tau_1$, whereas $\Delta I_1$ and $\Delta I_2$ in Eqs (24) and (25) are suppressed by the exchange splitting $4f_1$ between the singlet and triplet. For polycrystalline materials, the intensity change should be the combination of the three processes, $\Delta I_1 (i = 1, 2, 3)$, suggesting that multiple Lorentzen functions may be required to describe experimental data, as shown experimentally.

**Photoexcitation intensity dependence of MFE.** It is observed that the MFE in PL in CH$_3$NH$_3$PbI$_3$ is also dependent on the photoexcitation intensity. Only when the intensity reaches a certain threshold, does the MFE become significant. The line shape of MFE shrinks with the increase of the photoexcitation intensity and is eventually stabilized. To explain this unusual intensity dependence, we notice that the MFE, as shown in Fig. 5, is pronounced only when the Zeeman energy dominates over the exchange splitting. As a specific example, we consider the Faraday configuration, where the energy splitting between $\psi_1$ and $\psi_2$ is $4f_2$. This exchange is of short-range and related to the exciton envelope function $\Phi(r)$ at $r = 0$, i.e., when the electron and hole are at the same location. For the 1S state,

$$J_\perp \propto \Phi(r = 0)^2 = 2a_0^2,$$ (27)

where $a_0$ is the effective Bohr radius of the exciton, $a_0 = \hbar^2/e^2\mu$ with $\mu^{-1} = m_e^{-1} + m_h^{-1}$ being the effective mass of exciton.
A high-intensity photoexcitation creates many free electron-hole pairs, whose density can be estimated as \( N = \alpha I \tau_e / h\omega \), where \( \alpha \) is the absorption coefficient, \( \alpha \sim 10^4 \text{ cm}^{-1} \), for the CH\(_3\)NH\(_2\)PbI\(_3\), \( \tau_e \) is the carrier recombination lifetime, \( \tau_e \sim 10^{-3} \text{ s} \), and \( h\omega \) is the photon energy. These free electron-hole pairs will screen the Coulomb interaction, which can be modeled by the Debye-Hückel theory of ion gases. The Coulomb potential \( -e^2/4\pi\varepsilon_0 r \), in the presence of charged particles, is replaced by the potential \( U \) that satisfies the Poisson equation, \( \nabla^2 \psi = -e^2/e(4\pi\varepsilon_0) \), and the ground-state wave function in such a potential can be written as \( \psi(r) = \begin{pmatrix} \beta Q \end{pmatrix}^{3/2} e^{-\beta r} \), where the trial parameter \( \beta \) can be obtained by minimizing the ground state energy of Hamiltonian \( -\nabla^2/2\mu + U(r), E = \begin{pmatrix} 1 \end{pmatrix}(2/3)\beta^2 Q^2 h^2/\mu - \beta^4 e^2/\varepsilon Q(4\beta^2 + 4\beta + 1) \). The wave function \( \bar{\psi}(r) \), as compared to \( \psi(r) \), is more spread in space, and the exchange will be reduced by a factor

\[
J_{\perp}(Q) = \left| \bar{\psi}(0)/\psi(0) \right|^2 = (\beta h^2 e Q/e^2 \mu)^3.
\]

Figure 5 illustrates the screening effect. We see that as the intensity of photoexcitation increases, the exchange is greatly reduced. The MFE, meanwhile, becomes significant. After the carrier density reaches \( 10^{18} \text{ cm}^{-3} \), the exchange is so small that \( 4J_{\perp}(Q) \tau_e \ll 1 \), and the line shape in \( \Delta I \) is independent of exchange, and therefore the photoexcitation intensity.

**Diamagnetic effect on excitons.** So far we have considered only the 15 exciton states and neglected the diamagnetic effect on excitons. The diamagnetic effect originates from the orbital motions of electron and hole, and has been used to directly measure the exciton’s binding energy and effective mass. For free electrons and holes, an applied magnetic field can localized their orbital wave function normal to the magnetic field, forming the Landau levels with the magnetic length \( \sqrt{\hbar/eB} \). Since the anisotropy in effective mass for both electron and hole are relatively small, as shown in Fig. 2, we use isotropic effective masses, \( m_e = (m_0 m_0^2)^{1/3}, m_h = (m_0 m_0^2)^{1/3}, \) and \( \mu^{-1} = m_e^{-1} + m_h^{-1} \), to study the diamagnetic effect.

The diamagnetic response of excitons is far more complex than that of free electron-hole pairs, but offers more valuable information on excitons as well as constituent electrons and holes. Under a small magnetic field, the Coulomb interaction in an exciton is predominant and the diamagnetic effect can be studied by applying the perturbation theory to the hydrogen-like exciton wavefunctions. Such a perturbation must fail when the magnetic length \( \sqrt{\hbar/eH} \) becomes much smaller than the orbital radius of exciton, \( a_0 = \hbar^2/e(\mu^2) \). In this high-magnetic field regime, it is more appropriate to use the Landau levels as the starting point. A ratio,
\[ \gamma = \hbar \omega / 2R_b \] between the exciton cyclotron energy \( \hbar \omega \) and the exciton binding energy, \( R_b = \mu e/(2e^2 \hbar^2) \), can be used to distinguish the weak (\( \gamma < 1 \)) and strong (\( \gamma > 1 \)) magnetic-field regimes.

The Hamiltonian for the envelop function \( \Phi(r_\perp - r_\parallel) \) at \( K = 0 \) (\( K \) being the center-of-mass momentum of exciton) reads

\[
H_D = -\frac{1}{2\mu} \nabla^2 - \frac{e^2}{\epsilon r} - \frac{e}{2\epsilon} (m_e^{-1} - m_h^{-1}) B \cdot L + \frac{e^2 B^2 (x^2 + y^2)}{8\mu c^2},
\]

where \( L = -i \mathbf{\nabla} \) is the orbital angular momentum. While this Hamiltonian of exciton is similar as that of hydrogen atom in a magnetic field, the key difference is that the third term contains \( m_e^{-1} - m_h^{-1} \), the difference between electron and hole effective masses, which will reduce to \( \mu^{-1} \) in the hydrogen case.

To reliably solve the Hamiltonian for an arbitrary magnetic field, we employ two different basis sets. In low magnetic fields, by using \( a_0(R_b) \) as the length (energy) scale, \( H_D = -\nabla^2 - \frac{2}{\gamma^2} + \gamma \gamma L_z + \frac{\gamma^2}{\gamma^2} (1 - \sqrt{\frac{2\pi}{5}} Y_{20}(\theta, \phi)) \), where \( \gamma = m/m_e - m/m_h \) and \( Y_{lm} \) is spherical harmonic function. We choose the basis set as

\[
\Phi_{nlm}(r) = \frac{2}{n^2} \left[ \frac{(n + l + 1)!}{(n + l - l)!} \right] e^{-r/\gamma} \left( \frac{2r}{\gamma} \right)^l L_{n-1}^{l+1} \left( \frac{2r}{\gamma} \right) Y_{lm}(\theta, \phi),
\]

which are the eigenstates of \( H_D = -\nabla^2 - \frac{2}{\gamma^2} + \gamma \gamma L_z \) which are the eigenstates of parity and \( 2 \) as the energy scales \( H_D = -\nabla^2 - \frac{2}{\gamma^2} + \gamma \gamma L_z \) and the eigenfunctions of a spherical harmonic oscillator \( H_D = -\nabla^2 + r^2 \gamma^2 \)

\[
\Psi_{nlm}(r) = N_{nl} e^{-r^2/\gamma^2} L_{n-1}^{l+1} \left( \frac{r}{\gamma} \right) Y_{lm}(\theta, \phi),
\]

with \( N_{nl} = 2^{l+1/2} \Gamma(n+l+1/2)!/\Gamma(n+l)! \) are chosen to be another basis set. These basis sets, with correct characteristics of wave functions in the low- and high-field regimes, facilitate an analytical evaluation of the Hamiltonian matrix elements (see the Methods section). Moreover the basis sets are eigenstates of parity and \( L_z = m \), which are good quantum numbers of the Hamiltonian. We use large basis sets in both regimes, \( n, l \leq 20 \) for \( \Psi_{nlm} \) and \( n, l \leq 29 \) for \( \Psi_{nlm} \) and diagonalize the Hamiltonian to obtain the eigenstates. The large basis sets allow us to approach the intermediate \( \gamma \) in both \( \gamma < 1 \) and \( \gamma > 1 \) regimes so that the solutions from both ends are smoothly connected. In the limit of \( \gamma \rightarrow \infty \), the eigenstates become the Landau levels of free electron and hole.

In Fig. 6, we compare the theoretical results with recent cyclotron resonance experiment \( 23 \), using the effective masses of \( m_e = 0.223 m_0 \) and \( m_h = 0.188 m_0 \), and the binding energy of 16 meV. The agreement between theory and experiment is excellent. In addition, the pronounced absorption peaks above the 2000 cm\(^{-1} \) are attributed to the intermediate \( \gamma \) in both \( \gamma < 1 \) and \( \gamma > 1 \) regimes so that the solutions from both ends are smoothly connected. In the limit of \( \gamma \rightarrow \infty \), the eigenstates become the Landau levels of free electron and hole.

**Discussion**

The hybrid inorganic-organic perovskites have shown great promise in photovoltaic and many other important applications because of their outstanding transport, optical, and magneto-optical properties. To understand these applications, in this paper, we have constructed a reliable and accessible effective-mass model of the hybrid perovskites, which connects effective masses, Rashba splittings, and anisotropic g-factors of conduction and valence bands. Using this effective-mass model, we have elucidated the observed MFE in exciton PL and its dependence on photoexcitations and identified a new \( \Sigma_2 \) mechanism of MFE. We have also calculated the cyclotron resonance of excitons for arbitrarily strong magnetic fields and pointed out that excitonic states such as \( 3D_{2s} \) provide information on the difference in effective masses of electron and hole.

This effective-mass model is a foundation on which systematic models of electron-phonon coupling, carrier mobility, and other transport properties can be developed. Because of the concise expressions of SOC, Rashba effect, and g-factor, this model also facilitates studies of spin relaxation \( 34 \), spin Hall effect \( 35 \), and other magneto optical and spintronic phenomena.

**Methods**

**Expressions of \( H_A, H_B, \) and \( H_C \).** The three \( 4 \times 4 \) matrices in Eq. (7) are displayed as
Figure 6. Cyclotron resonance of excitons in CH$_3$NH$_3$PbI$_3$. Solid lines are energies of different exciton states. Dashed lines are the energy difference between the Landau levels of free electron and holes with (N, N) being the Landau-level index. Dots are the experimental data from ref. 23. The absorption peak between 2S and (1, 1) coincides with the energies of 3D$_{1,2}$ states.

$$H_A = \begin{pmatrix}
E_v + \frac{eB_z}{2mc} & \frac{eB_z}{2mc} & -\sin\xi (iP k_z + \zeta) & -i \cos\xi P k_z \\
E_v - \frac{eB_z}{2mc} & -i \cos\xi P k_z & \sin(\zeta (iP k_z + \zeta)) & \\
E_e + A_x k_x^2 + B_x k_x^2 & S_{\perp}^0 \frac{eB_z}{4mc} & S_{\perp}^0 \frac{eB_z}{4mc} & \\
E_e + A_x k_x^2 + B_x k_x^2 - S_{\perp}^0 \frac{eB_z}{4mc} & \\
\end{pmatrix}$$  

where

$$A_x = \frac{L_1 + M_1}{2} \cos^2\xi + M_1 \sin^2\xi, B_x = L_2 \sin^2\xi + M_2 \cos^2\xi,$$

$$S_{\perp}^0 = 2 \left( \frac{3\xi_1 + 2}{2 \sin^2\xi + \frac{1}{2}} \right), S_{\perp}^0 = 2 \left( \frac{3\xi_2 + 1}{2} \sin^2\xi - \frac{1}{2} \sin^2\xi \right),$$

$$k_x^2 = k_x^2 + k_y^2, k_x = \frac{1}{\sqrt{2}} (k_x \pm ik_y), B_x = B_y \pm iB_y.$$

$$H_B = \begin{pmatrix}
-iP k_z & 0 & \cos(\zeta (iP k_z + d)) & i \sin(\zeta P k_z) \\
0 & iP k_z & -i \sin(\zeta P k_z) & \cos(\zeta (iP k_z + d)) \\
\sin(\zeta N_x k_x + z_x) \frac{eB_z}{2mc} & U_1 \cos\xi & U_2 + Z_2 \frac{eB_z}{2mc} & -N_x k_x z_x + Z_2 \frac{eB_z}{2mc} \\
-U_1^* \cos\xi & \sin(\zeta N_x k_x - z_x) \frac{eB_z}{2mc} & -N_x k_x - Z_2 \frac{eB_z}{2mc} & U_2 + Z_2 \frac{eB_z}{2mc} \\
\end{pmatrix}$$  

where

$$Z_1 = \frac{1}{2} \cos\xi + \frac{3\xi_2 + 1}{2\sqrt{2}} \sin\xi,$$

$$Z_2 = -\frac{3}{2} (\xi_1 + 1) \sin\xi \cos\xi,$$

$$Z_3 = -\frac{1}{2} \sin\xi \cos\xi + \frac{3\xi_2 + 1}{2\sqrt{2}} (\sin^2\xi - \cos^2\xi),$$

$$U_1 = -\frac{1}{2} \left( L_1 - M_1 \right) (k_x^2 - k_y^2) - 2iN_x k_x k_y,$$

$$U_2 = \sin\xi \cos\xi \left( \frac{L_1 + M_1}{2} - M_3 \right) k_x^2 - (L_2 - M_2) k_x^2.$$
\[
\begin{bmatrix}
A_\epsilon k^2 + B_\epsilon k^2 - \frac{g}{2} \sigma_x' - \cos \theta \sigma_y' + Z_1 \sin \theta & 0 \\
A_\epsilon k^2 + B_\epsilon k^2 - \frac{g}{2} \sigma_x' + \cos \theta \sigma_y' + Z_1 \sin \theta & A_\epsilon k^2 + B_\epsilon k^2 + \frac{g}{2} \sigma_x' + \cos \theta \sigma_y' + Z_1 \sin \theta
\end{bmatrix}
\]

where

\[
A_\epsilon' = \frac{L_1 + M_1}{2}, \quad B_\epsilon' = M_2
\]

\[
A_\epsilon = \frac{L_1 + M_1}{2} \sin^2 \xi + M_2 \cos^2 \xi, \quad B_\epsilon = L_2 \cos^2 \xi + M_2 \sin^2 \xi
\]

\[
Z_4 = \frac{1}{2} \sin \xi - \frac{3}{2} \cos \xi
\]

\[
Z_5 = \frac{1}{2} \cos^2 \xi - \frac{3}{2} \sin \xi
\]

\[
Z_6 = \frac{1}{2} \cos^2 \xi - \frac{3}{2} \sin \xi \cos \xi
\]

### Derivations of Eq. (15)

When the applied magnetic field \( B \) tilts away from the crystal C-axis with an angle \( \theta \), we can define the new z-axis (denoted \( \hat{z}' \)) along \( B \) and assume that the tilting is in the x-z plane with the new x-axis denoted as \( \hat{x}' \). The transformations of coordinates between the two references are

\[
\sigma_x' = \cos \theta \sigma_x - \sin \theta \sigma_z, \quad \sigma_y' = \cos \theta \sigma_y, \quad \sigma_z' = \sigma_z
\]

\[
k_x' = \cos \theta k_x - \sin \theta k_z, \quad k_y' = \sin \theta k_x + \cos \theta k_z
\]

The Zeeman energy in Eqs (9) and (10) then becomes

\[
H_Z = \frac{\hbar}{2} B \left( (g_\| \cos^2 \theta + g_\perp \sin^2 \theta) \sigma'_x + (g_\perp - g_\|) \sigma'_y \sin \theta \cos \theta \right)
\]

and the effective g-factor \( g(\theta) \) in Eq. (15) can be obtained by diagonalizing this Hamiltonian.

In the new reference system, \( \{ k'_x, k'_y \} = -i eB/\hbar c \), and the kinetic energy in Eqs (9) and (10) reads

\[
E_k = A k_x'^2 + B k_y'^2 + C k_z'^2 + D k_x' k_z'
\]

with \( A = \frac{\hbar^2}{2 m_1} \cos^2 \theta + \frac{\hbar^2}{2 m_2} \sin^2 \theta \), \( B = \frac{\hbar^2}{2 m_1} C = \frac{\hbar^2}{2 m_2} \sin^2 \theta + \frac{\hbar^2}{2 m_2} \cos^2 \theta \), \( D = \frac{\hbar^2}{2 m_2} - \frac{\hbar^2}{2 m_1} \sin \theta \cos \theta \). We can define the ladder operators \( b \) and \( b^+ \) of the Landau levels as

\[
b = \frac{l_B}{\sqrt{2}(AB)^{1/4}} \left( \sqrt{A} k_x' + i \sqrt{B} k_y' + \frac{D}{\sqrt{A}} k_z' \right), \quad b^+ = \frac{l_B}{\sqrt{2}(AB)^{1/4}} \left( \sqrt{A} k_x' - i \sqrt{B} k_y' + \frac{D}{\sqrt{A}} k_z' \right)
\]

with \( l_B = \sqrt{\frac{eB}{\hbar c}} \), which satisfy \( [b, b^+] = 1 \). The kinetic energy is then expressed as

\[
E_k = 2 \sqrt{\frac{AB}{hc}} \left( b^* b + \frac{1}{2} \right) + \left( C - \frac{D^2}{A} \right) k_z'^2
\]

with \( \sqrt{\frac{AB}{hc}} = \frac{\hbar^2}{m_1} \left( \cos^2 \theta + \frac{m_2}{m_1} \sin^2 \theta \right)^{1/2} \), which gives \( m_i(\theta) \) in Eq. (15).

### Matrix elements of \( H_0 \) in basis sets of \( \Phi_{nlm} \) and \( \Psi_{nlm} \)

The matrix elements of \( H_0 \) among \( \Phi_{nlm} \) and among \( \Psi_{nlm} \) can be evaluated analytically, which greatly simplifies the eigenstate calculations.

The matrix element of angle-dependent term in the Hamiltonian can be calculated via the integral

\[
\int Y_l^m Y_{2\ell} Y_{l'} Y_{l'm'} d\Omega = (-1)^{m_1} [(2l_1 + 1)(2l_2 + 1)]^{1/2} \left[ \frac{5}{4\pi} \right]^{1/2} \left[ \begin{array}{c} 1 \ell \ell \ell \\ 0 0 0 \end{array} \right] \left[ \begin{array}{c} l_1 \ell_1 \ell_2 \\ 0 \end{array} \right] \left[ \begin{array}{c} \ell_1 \ell_1 \ell_2 \\ -m_1 \ell_1 \ell_2 \end{array} \right],
\]

where the Wigner 3-j symbols are used.

The only type of matrix elements to be evaluated is \( r' \) between the basis functions. Between basis functions \( \Phi_{n,l,m} \) and \( \Phi_{n',l',m'} \),
\[
(r^n)_{ij} \propto \int_0^\infty r^{l_j+l+2} e^{-r} \left( \frac{1}{n_i} + \frac{1}{n_j} \right) r^{2l_{j-1}} \left( \frac{2r}{n_i} \right) r^{2l_{i-1}} \left( \frac{2r}{n_j} \right) dr.
\]

The integral can be worked out analytically,

\[
\int_0^\infty \cdots dr = \frac{\Gamma(\gamma)}{\sigma^{n+m+1}} \left( \frac{m + \alpha}{n - k} \right) \left( \frac{k + \gamma}{\lambda} \right) \times 2F_1 \left[ -m + k, \gamma + k + 1, \alpha + k + 1; \frac{\lambda}{\sigma} \right]
\]

\[
\times 2F_1 \left[ -n + k, \gamma + k + 1, \beta + k + 1; \frac{\mu}{\sigma} \right]
\]

where \( \gamma = l_i + l_j + 2, \sigma = \frac{1}{n_i} + \frac{1}{n_j}, \alpha = 2l_i + 1, \beta = 2l_j + 1, m = n_i - l_i - 1, n = n_j - l_j - 1, \lambda = 2/\mu, \mu = 2/\eta, \) and \( 2F_1(\alpha, \beta, \gamma, z) \) is the Gauss' hypergeometric function.

The matrix element of \( r^n \) between basis functions \( \Psi_{nl,lm} \) and \( \Psi_{m'n',l'm'} \), neglecting the normalization factor, is

\[
\int_0^\infty r^{l_i+l_j+2} e^{-r} L_{n_i}^{l_i+1} \left( \frac{1}{r} \right) L_{n_j}^{l_j+1} \left( \frac{1}{r} \right) dr
\]

\[
= \Gamma \left( \frac{l_i + l_j + s + 3}{2} \right) \sum_{k=0}^{\min(n_i,n_j)} \left( \begin{array}{c} n_j + l_j - \frac{1}{2} \left( n_j + l_j + 1 \right) \\ n_j - k \end{array} \right) \times \left( \begin{array}{c} k + \frac{1}{2} (l_i + l_j + s + 1) \\ l_i \end{array} \right) \times 2F_1 \left[ -n_j + k, \frac{1}{2} (l_i + l_j + s + 3) + k, l_j + k + \frac{3}{2}; 1 \right]
\]

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**Author Contributions**

Z.G.Y. conceived the concept, performed the calculations, analyzed the results and wrote the manuscript.

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