

Supporting information for:

Theory and *Ab Initio* Computation of the Anisotropic Light Emission in Monolayer Transition Metal Dichalcogenides

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Derivation of the Exciton Radiative Decay Rate

To calculate the exciton decay rate, we consider the transition between an initial state $|SQ, 0\rangle$ consisting of an exciton in state S with momentum \mathbf{Q} and no photons, to a final state $|G, 1_{\lambda\mathbf{q}}\rangle$, where G is the electronic ground state and $1_{\mathbf{q}}$ denotes a photon with polarization λ and wavevector \mathbf{q} . The transition is accompanied by the emission of a photon, and is

mediated by the minimal coupling interaction Hamiltonian:

$$H^{\text{int}} = \frac{e}{m} \mathbf{A} \cdot \mathbf{p} ; \quad \mathbf{A} = \sum_{\mathbf{q}} \sqrt{\frac{\hbar}{2\omega_{\mathbf{q}} V \epsilon_0}} \mathbf{e}_{\mathbf{q}} (\hat{a}_{\mathbf{q}}^{\dagger} e^{-i\mathbf{q} \cdot \mathbf{r}} + \hat{a}_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}}), \quad (1)$$

where V is the volume of the system, $\mathbf{e}_{\mathbf{q}}$ are the photon polarization unit vectors, and $\hat{a}_{\mathbf{q}}$ and $\hat{a}_{\mathbf{q}}^{\dagger}$ are the photon annihilation and creation operators, respectively. SI units are used here and below. We employ Fermi's Golden Rule to compute the exciton radiative decay rate:

$$\begin{aligned} \gamma_S(\mathbf{Q}) &= \frac{2\pi}{\hbar} \sum_{\lambda \mathbf{q}}^{\{(\mathbf{q} \cdot \hat{\mathbf{Q}}) \hat{\mathbf{Q}} = \mathbf{Q}\}} \left| \langle G, 1_{\lambda \mathbf{q}} | H^{\text{int}} | S\mathbf{Q}, 0 \rangle \right|^2 \delta(E_S(\mathbf{Q}) - \hbar c q) \\ &= \frac{\pi e^2}{\epsilon_0 m^2 c V} \sum_{\lambda \mathbf{q}}^{\{(\mathbf{q} \cdot \hat{\mathbf{Q}}) \hat{\mathbf{Q}} = \mathbf{Q}\}} \frac{1}{q} |\mathbf{e}_{\mathbf{q}} \cdot \langle G | \mathbf{p} | S\mathbf{Q} \rangle|^2 \delta(E_S(\mathbf{Q}) - \hbar c q), \end{aligned} \quad (2)$$

where we approximated $e^{-i\mathbf{q} \cdot \mathbf{r}} \approx 1$ since the photon momentum is small. The sum runs over two polarizations and the delta expresses energy conservation. Since we focus on monolayer materials, the exciton has a 2D character, so that we can write its momentum as $\mathbf{Q} = Q_x \hat{\mathbf{x}} + Q_y \hat{\mathbf{y}}$ when the material is contained in the xy plane. Momentum conservation then requires that the in-plane component of the emitted photon wavevector be equal to \mathbf{Q} , namely, $(\mathbf{q} \cdot \hat{\mathbf{Q}}) \hat{\mathbf{Q}} = \mathbf{Q}$ (see Figure 1 of the main text); this constraint is noted in curly brackets in the summation of eq 2. As explained in the main text, we approximate the transition dipole matrix element as the 2D vector $\mathbf{p}_S = \langle G | \mathbf{p} | S\mathbf{Q} \rangle = p_{Sx} \hat{\mathbf{x}} + p_{Sy} \hat{\mathbf{y}}$ with complex-valued components p_{Sx} and p_{Sy} . As noted in the main text, we use the velocity operator, and compute the transition dipole as $\mathbf{p}_S(\mathbf{Q}) = (-im/\hbar) \langle G | [\mathbf{x}, H] | S\mathbf{Q} \rangle$ to correctly include the non-local part of the Hamiltonian.

To evaluate eq 2, we write the exciton momentum as $\mathbf{Q} = Q \cos \varphi \hat{\mathbf{x}} + Q \sin \varphi \hat{\mathbf{y}}$ and, without loss of generality, sum over the IP and OOP photon polarization vectors defined in the main text. Taking the continuous limit of the summation over the photon wavevector, using A for the area of the system and L_z for its length along z (so that $V = A \cdot L_z$), and

imposing the constraint $q^2 = Q^2 + q_z^2$ inside the delta function, we obtain eq 4 of the main text:

$$\begin{aligned}
& \gamma_S(\mathbf{Q}) \\
&= \frac{\pi e^2}{\epsilon_0 m^2 c V} \frac{L_z}{2\pi} \int_{-\infty}^{\infty} \frac{dq_z}{q} \left(\left| -p_{Sx} \sin \varphi + p_{Sy} \cos \varphi \right|_{\text{IP}}^2 \right. \\
&\quad \left. + (\cos^2 \theta) \left| p_{Sx} \cos \varphi + p_{Sy} \sin \varphi \right|_{\text{OOP}}^2 \right) \delta(E_S(\mathbf{Q}) - \hbar c q) \\
&= \frac{e^2 p_S^2}{2\epsilon_0 m^2 c A} 2 \int_0^{\infty} \frac{dq_z}{q} \left(\left| -\frac{p_{Sx}}{p_S} \sin \varphi + \frac{p_{Sy}}{p_S} \cos \varphi \right|_{\text{IP}}^2 \right. \\
&\quad \left. + \frac{q_z^2}{q^2} \left| \frac{p_{Sx}}{p_S} \cos \varphi + \frac{p_{Sy}}{p_S} \sin \varphi \right|_{\text{OOP}}^2 \right) \delta \left(\frac{E_S(\mathbf{Q})}{\hbar c} - \sqrt{q_z^2 + Q^2} \right) \\
&= \frac{e^2 p_S^2}{\epsilon_0 m^2 c A} \cdot \int_Q^{\infty} \frac{dq}{\sqrt{q^2 - Q^2}} \left(\left| -\frac{p_{Sx}}{p_S} \sin \varphi + \frac{p_{Sy}}{p_S} \cos \varphi \right|_{\text{IP}}^2 \right. \\
&\quad \left. + \frac{q^2 - Q^2}{q^2} \left| \frac{p_{Sx}}{p_S} \cos \varphi + \frac{p_{Sy}}{p_S} \sin \varphi \right|_{\text{OOP}}^2 \right) \delta \left(\frac{E_S(\mathbf{Q})}{\hbar c} - q \right) \\
&= \gamma_S(0) \cdot \left(\frac{E_S(0)}{\sqrt{E_S^2(Q) - \hbar^2 c^2 Q^2}} \right) \left\{ \left| -\frac{p_{Sx}}{p_S} \sin \varphi + \frac{p_{Sy}}{p_S} \cos \varphi \right|_{\text{IP}}^2 \right. \\
&\quad \left. + \frac{E_S(Q)^2 - \hbar^2 c^2 Q^2}{E_S(Q)^2} \left| \frac{p_{Sx}}{p_S} \cos \varphi + \frac{p_{Sy}}{p_S} \sin \varphi \right|_{\text{OOP}}^2 \right\} \tag{3}
\end{aligned}$$

Angular dependence of the radiative rate

To compute the PL intensity emitted as a function of angle by an exciton S upon recombination, we first substitute

$$\frac{\sqrt{E_S^2(Q) - \hbar^2 c^2 Q^2}}{E_S(0)} \approx \frac{\sqrt{E_S^2(Q) - \hbar^2 c^2 Q^2}}{E_S(Q)} = \cos \theta$$

in eq (4) of the main text, and obtain:

$$\gamma_S(\mathbf{Q}) = \frac{\gamma_S(0)}{\cos \theta} \cdot \left\{ \left| -\frac{p_{Sx}}{p_S} \sin \varphi + \frac{p_{Sy}}{p_S} \cos \varphi \right|_{\text{IP}}^2 + \cos^2 \theta \left| \frac{p_{Sx}}{p_S} \cos \varphi + \frac{p_{Sy}}{p_S} \sin \varphi \right|_{\text{OOP}}^2 \right\}. \quad (4)$$

Guided by Figure S1 below, we then convert $\gamma_S(\mathbf{Q})$ to $\gamma_S(\theta, \varphi)$, as follows. For an exciton in state S and with center-of-mass momentum \mathbf{Q} located around a small area $dA_{\mathbf{Q}}$ in phase space, the emission occurs over a small solid angle spanned by the area dA_{θ} . One can thus write:

$$\gamma_S(\theta, \varphi) dA_{\theta} = \gamma_S(\mathbf{Q}) dA_{\mathbf{Q}}. \quad (5)$$

Using $dA_{\mathbf{Q}} = Q dQ d\varphi$ as well as $dA_{\theta} = q^2 \sin \theta d\theta d\varphi$, as seen in Figure S1, together with $Q = q \sin \theta$, we obtain:

$$\gamma_S(\theta, \varphi) = \gamma_S(\mathbf{Q}) \cos \theta. \quad (6)$$

Using eq 4, we finally obtain:

$$\gamma_S(\theta, \varphi) = \gamma_S(0) \cdot \left\{ \left| -\frac{p_{Sx}}{p_S} \sin \varphi + \frac{p_{Sy}}{p_S} \cos \varphi \right|_{\text{IP}}^2 + \cos^2 \theta \left| \frac{p_{Sx}}{p_S} \cos \varphi + \frac{p_{Sy}}{p_S} \sin \varphi \right|_{\text{OOP}}^2 \right\}. \quad (7)$$

This result is given in Eqs. (6-7) of the main text, where the IP and OOP rates are given separately.

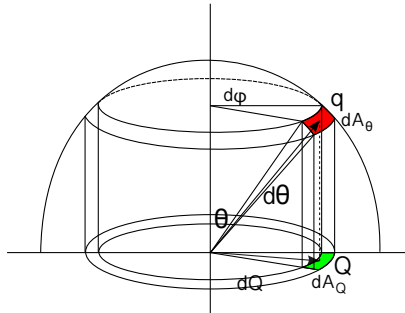


Figure S1: An exciton associated with the phase space area $dA_{\mathbf{Q}}$ (shown in green) decays radiatively by emitting a photon through the area dA_{θ} (shown in red).

Temperature dependence of the radiative rate

To obtain the exciton radiative rate at temperature T , we average the rate using a parabolic exciton dispersion:

$$E_S(\mathbf{Q}) = E_S(0) + \frac{\hbar^2 Q^2}{2M_S} \quad (8)$$

where M_S is the exciton effective mass, which is defined as the sum of the electron and hole effective masses. Note that only excitons inside the light cone can decay radiatively, so that the integration range is limited by an upper exciton momentum Q_0 , which satisfies the light-cone condition:

$$\hbar c Q_0 = E_S(0) + \frac{\hbar^2 Q_0^2}{2M_S}. \quad (9)$$

As a result, for a given exciton state S , we can take the thermal average of the radiative decay rate along a fixed direction defined by the angle φ :

$$\begin{aligned} \langle \gamma_S \rangle(\varphi, T) &= \frac{1}{Z} \int_0^{Q_0} dQ Q e^{-\hbar^2 Q^2 / 2M_S k_B T} \frac{\gamma_S(0) E_S(0)}{\sqrt{E_S^2(Q)^2 - \hbar^2 c^2 Q^2}} \\ &\quad \times \left[\left| -\frac{p_{Sx}}{p_S} \sin \varphi + \frac{p_{Sy}}{p_S} \cos \varphi \right|^2 + \frac{E_S(Q)^2 - \hbar^2 c^2 Q^2}{E_S(Q)^2} \left| \frac{p_{Sx}}{p_S} \cos \varphi + \frac{p_{Sy}}{p_S} \sin \varphi \right|^2 \right] \\ &\quad \frac{\int_0^{Q_0^2} dQ^2 \left[\frac{\left| -\frac{p_{Sx}}{p_S} \sin \varphi + \frac{p_{Sy}}{p_S} \cos \varphi \right|^2}{\sqrt{1 - \hbar^2 c^2 Q^2 / E_S^2(0)}} + \sqrt{1 - \hbar^2 c^2 Q^2 / E_S^2(0)} \left| \frac{p_{Sx}}{p_S} \cos \varphi + \frac{p_{Sy}}{p_S} \sin \varphi \right|^2 \right]}{2M_S k_B T / \hbar^2} \\ &\approx \gamma_S(0) \left(\frac{E_S(0)^2}{2M_S c^2 k_B T} \right) \left[2 \left| -\frac{p_{Sx}}{p_S} \sin \varphi + \frac{p_{Sy}}{p_S} \cos \varphi \right|^2 + \frac{2}{3} \left| \frac{p_{Sx}}{p_S} \cos \varphi + \frac{p_{Sy}}{p_S} \sin \varphi \right|^2 \right] \\ &= \gamma_S(0) \left(\frac{E_S(0)^2}{2M_S c^2 k_B T} \right) \left[\left| \frac{p_{Sx}}{p_S} \right|^2 \left(\frac{2}{3} + \frac{4}{3} \sin^2 \varphi \right) + \left| \frac{p_{Sy}}{p_S} \right|^2 \left(\frac{2}{3} + \frac{4}{3} \cos^2 \varphi \right) \right. \\ &\quad \left. - \frac{2}{3} \left(\frac{p_{Sx}^* p_{Sy} + p_{Sx} p_{Sy}^*}{p_S^2} \right) \sin 2\varphi \right], \quad (10) \end{aligned}$$

where the partition function

$$Z = \int_0^\infty dQ Q e^{-\hbar^2 Q^2 / 2M_S k_B T}, \quad (11)$$

and to compute the numerator we made the physically justified approximations $E_S(Q) \approx E_S(0)$ and $Q_0 \approx E_S(0)/\hbar c$.

As a last step, we average $\langle \gamma_S \rangle(\varphi, T)$ over the emission angle φ and take the inverse to obtain the radiative lifetime in eq 11 of the main text:

$$\langle \tau_S \rangle(T) = \left[\int_0^{2\pi} \frac{d\varphi}{2\pi} \langle \gamma_S \rangle(\varphi, T) \right]^{-1} = \gamma_S^{-1}(0) \cdot \frac{3}{4} \left(\frac{E_S(0)^2}{2M_S c^2 k_B T} \right)^{-1}. \quad (12)$$