First-Principles Many-Body Theory and Quantum Dynamics for Materials in Quantum Information Science

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Abstract: Stable, scalable, and reliable quantum information science (QIS) is poised to revolutionize human well-being through quantum computation, communication and sensing. Here, I show our recent development on first-principles computational platforms to study quantum coherence and optical readout as critical processes in QIS in solid-state materials, by combining first-principles many-body theory and open quantum dynamics. First, we show how we reliably predict energetics, electronic and optical properties of spin defects and their host two-dimensional(2D) materials from first-principles many-body theory, which accurately describes highly anisotropic dielectric screening and strong many-body interactions. In particular, we show how we identify the chemical composition of single photon emitters in hexagonal boron nitride and 2D magnet $NiPS_3$ by computing optical transitions, radiative and nonradiative as well as intersystem crossing kinetic rates with strong exciton-defect couplings from first-principles. Next, we introduce our recently developed real-time density-matrix dynamics approach with first-principles electron-electron, electron-phonon, electron-impurity scatterings and self-consistent spin-orbit coupling, which can accurately predict spin and carrier lifetime and pump-probe Kerr-rotation signatures for general solids. As an example, we will show our theoretical prediction on Dirac materials under electric field with extremely long spin lifetime and spin diffusion length and spin relaxation in bulk halide perovskite. This theoretical and computational development is critical for designing new materials promising in quantum-information science, spintronics, and valleytronics applications.

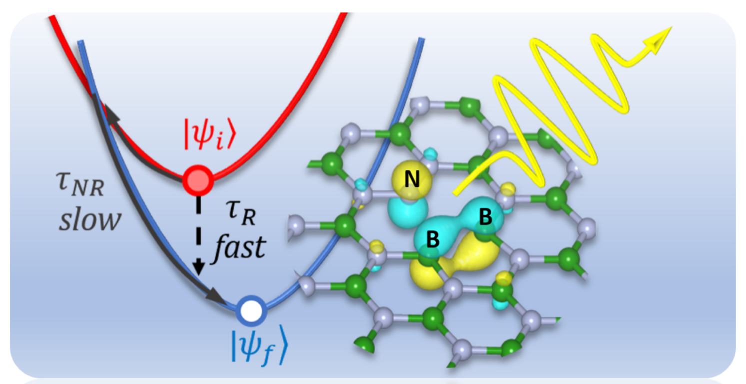
Spin Defects for Quantum Information

Theory Design – Defects based Qubits and Single Photon Emitters

- **Deep defect levels**
- **Bright optical transitions**
- **High spin state**
- **High quantum yield and PL contrast**
- **Long spin relaxation and coherence time**

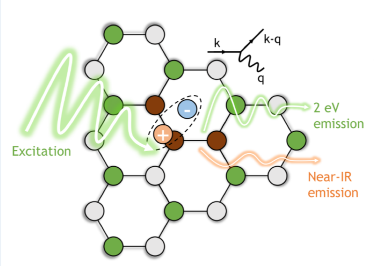
First-Principles – Methodology Development

- **Many-body theory –** include screened Coulomb interaction (GW)[1,2,3,4]
- **Exciton recombination –** solving the Bethe-Salpeter Equation (BSE)[3,4,5]
- **Substrate screening –** polarizability including implicit substrate[6,11]
- **Charged cell correction for 2D –** including dielectric function $\epsilon(z)$[1,2,7]
- **Spin-lattice relaxation time –** ab-initio density matrix dynamics with SOC & e-ph[8,12,13]
- **Nonradiative recombination –** phonon mediated recombination[9]



Identification of SPE in hBN

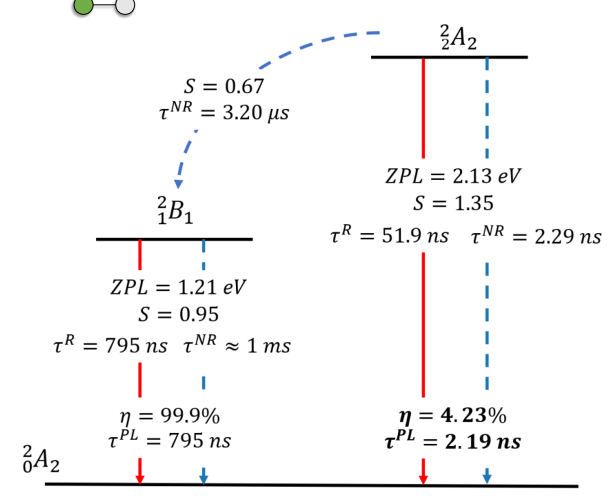
Carbon trimer (C_2C_N)[5] as 2 eV SPE candidate predicted from first-principles

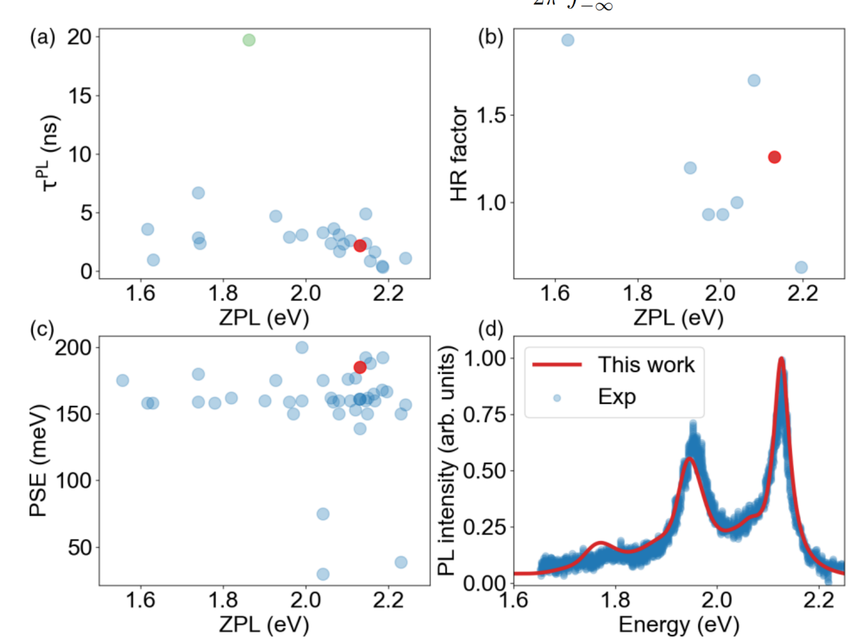


$$\tau^{PL} = 1/\left(\frac{1}{\tau^R} + \sum_i \frac{1}{\tau_i^{NR}}\right) = \tau^R * \eta$$

$$\eta = \frac{1}{\tau^R}/\left(\frac{1}{\tau^R} + \sum_i \frac{1}{\tau_i^{NR}}\right)$$

PL line shape: $A(E_{ZPL} - \hbar\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} G(t)e^{i\omega t - \gamma|t|}dt$





Radiative and Nonradiative Recombination

Radiative Recombination[9]

We compute the radiative recombination including excitonic effects for N_BV_N

$$\gamma(\vec{Q}) = \frac{2\pi}{\hbar}\frac{2\pi e^2}{m^2 cV\hbar q}\left|\epsilon_{\vec{q}\lambda}\cdot\langle G|\vec{r}|S\rangle\right|^2\delta(E(\vec{Q}) - \hbar cq)$$

$$r^{0D}(\boldsymbol{Q} = 0) = \frac{4e^2}{3\hbar c^3}\Omega_0^3\mu_A^2$$

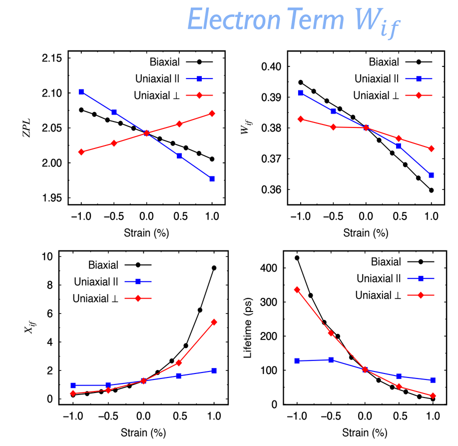
Isolated limit

DFT-RPA (ns)	GW-BSE (ns)
64	36

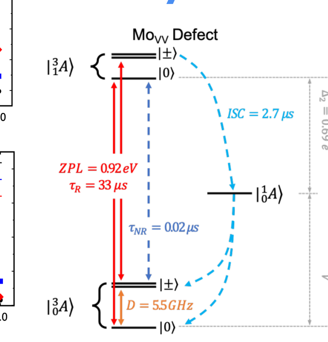
Nonradiative Recombination[9]

$$r_{if} = \frac{2\pi}{\hbar}\left|\left\langle\psi_f(r,R_a)\left|\frac{\partial H}{\partial Q}\right|\psi_i(r,R_a)\right\rangle\right|^2\sum_n p(i,n)\sum_m\left|\langle\phi_{in}(Q)|(Q - Q_a)|\phi_{fm}(Q)\rangle\right|^2\delta(m\hbar\omega_f - n\hbar\omega_i - \Delta E_{if})$$

Electron Term W_{if} Phonon Term X_{if} $X_{if}(S, ZPL, \hbar\omega) \sim e^{-S}S^{\frac{ZPL}{\hbar\omega}}/\left(\frac{ZPL}{\hbar\omega}\right)!$

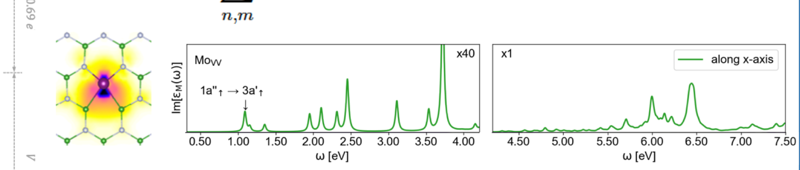


Intersystem crossing (ISC)[10]



$\Gamma_{ISC} = 4\pi\hbar\lambda_\perp^2\widetilde{X}_{if}(T)$ Spin-orbit coupling constant: $\lambda_\perp$

$$\widetilde{X}_{if}(T) = \sum_{n,m} p_{in}\left|\langle\phi_{fm}(\mathbf{R})|\phi_{in}(\mathbf{R})\rangle\right|^2\delta(m\hbar\omega_f - n\hbar\omega_i + \Delta E_{if})$$



Exciton $\psi_{e,h}$ of Mo_{vv} in hBN by solving BSE

Ab-initio Density-Matrix Dynamics

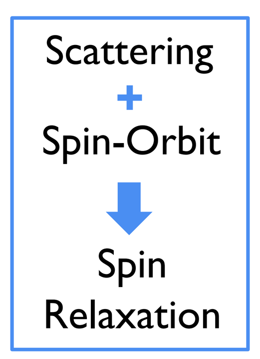
Real-time Dynamics and Density Matrix Evolution[8,12]

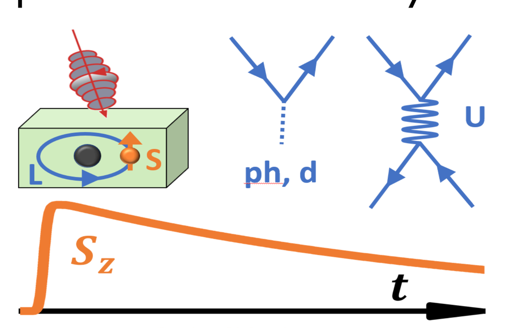
$$i\hbar\dot{\rho} = [H,\rho] + F[\rho]$$

e-photon, B, E field

e-e, e-imp, e-ph

Physical processes involved in dynamics





Spin lifetime τ_s

$S = \mathrm{Tr}(\rho s) = S_0 e^{-t/\tau_s}$

No experimental / fitting parameters

"A universal model of spin relaxation in solids", Physics Magazine, 2021

Lindblad dynamics for scattering

The scattering term reads

$$\left.\frac{d\rho_{12}}{dt}\right|_c = \frac{1}{2}\sum_{345}\begin{bmatrix}(I-\rho)_{13}P^c_{32,45}\rho_{45} \\ -(I-\rho)_{45}P^{c,*}_{45,13}\rho_{32}\end{bmatrix} + \mathrm{H.c.}$$

For electron-phonon scattering,

$$P^{S,e\text{-}ph}_{1234} = \sum_{q\lambda\pm}A^{q\lambda\pm}_{13}A^{q\lambda\pm,*}_{24}$$

$$A^{q\lambda\pm}_{13} = \sqrt{\frac{2\pi}{\hbar}}g^{q\lambda\pm}_{12}\sqrt{\delta^G_\sigma(\epsilon_1 - \epsilon_2 \pm \omega_{q\lambda})}\sqrt{n^\pm_{q\lambda}}$$

"S" means Schrodinger Picture; g_{12} is e-ph coupling matrix with SOC

References

[1] T. J. Smart, F. Wu, M. Govoni, and Y. Ping, Phys. Rev. Mat. 2, 124002 (2018)

[2] F. Wu, A. Galatas, R. Sundararaman, D. Rocca, and Y. Ping, Phys. Rev. Mater. 1, 071001(R) (2017)

[3] Y. Ping, D. Rocca, and G. Galli, Chem. Soc. Rev. 42, 2437 (2013)

[4] F. Wu, D. Rocca, Y. Ping, J. Mater. Chem. C, **7**, 12891, (2019)

[5] K. Li, T. Smart, and Y. Ping, Phys. Rev. Mater., 6, L042201 (2022), *Editor's suggestions.*

[6] C. Guo, J. Xu, D. Rocca, and Y. Ping, Phys. Rev. B, 102, 205113, (2020), *Editor's suggestions.*

[7] R. Sundararaman, and Y. Ping, J. Chem. Phys., 146, 104109 (2017)

[8] J. Xu, A. Habib, F. Wu, S. Kumar, R. Sundararaman, and Y. Ping, Nat. Commun., 11, 2780, (2020)

[9] F. Wu, T. J. Smart, and Y. Ping, Phys. Rev. B, 100, 081407(R) (2019)

[10] T. Smart, K. Li, J. Xu and Y. Ping, npj Comput. Mater. 7, 59 (2021)

[11] C. Guo, J. Xu and Y. Ping, J. of Phys.: Condens. Matter, 33, 234001, (2021), *Emerging leaders issue.*

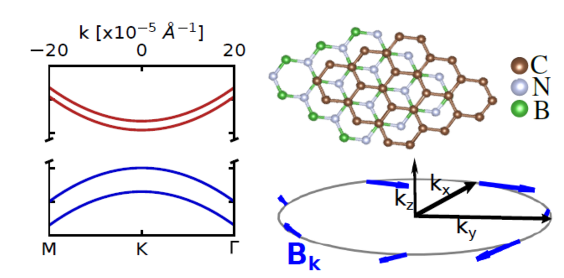
[12] J. Xu, A. Habib, R. Sundararaman, Y. Ping, Phys. Rev. B 104, 184418 (2021), *Editor's suggestions.*

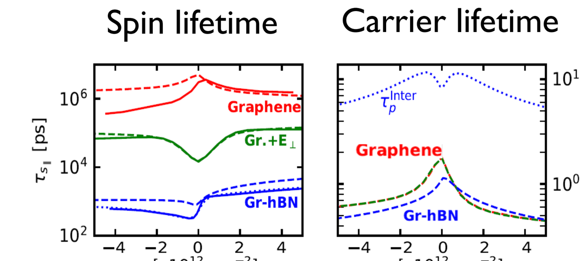
[13] A. Habib, J. Xu, Y. Ping and R. Sundararaman, Phys. Rev. B 105, 115122 (2022)

[14] J. Xu, H. Takenaka, A. Habib, R. Sundararaman, Y. Ping, Nano Lett. 21, 9594 (2021)

Spin Relaxation and Dynamics in 2D Materials

Graphene on a clean hBN substrate[13]

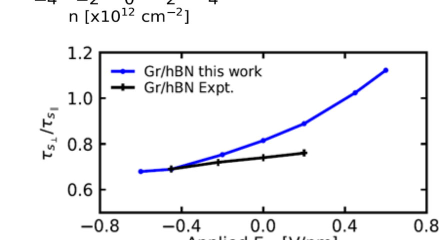




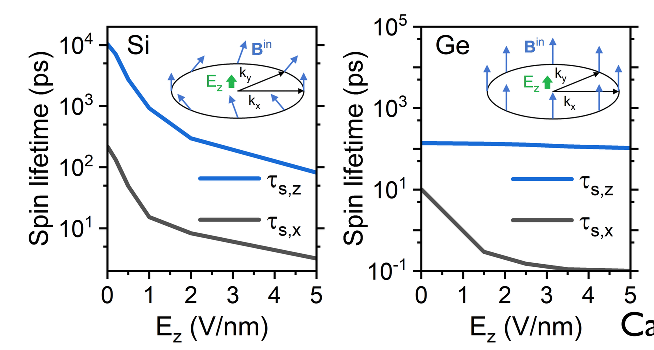
n > 0: elec. Density; n < 0: hole density

- ❑ Spin-phonon scattering was thought unimportant
- ❑ Our simulations show substrate effects can well explain two phenomena: (i) electron-hole asymmetry; (ii) $\frac{\tau_{s,\perp}}{\tau_{s,\parallel}} > 0.5$

Anisotropy



Graphene derivatives with strong SOC- silicene and germanene[14]



Left figure: τ_s at 300 K as a function of E_z

- ❑ Spin lifetimes are highly anisotropic
- ❑ $\tau_{s,z}$ of Silicene and Germanene have different responses to electric field

← Different spin relaxation mechanisms

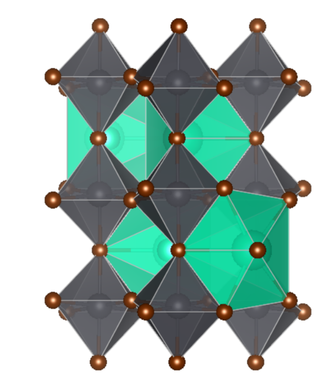
Predicted spin diffusion length l_s of Ge > The exp. values of graphene samples 1-30 μm

Calculated transport properties of Germanene with defects

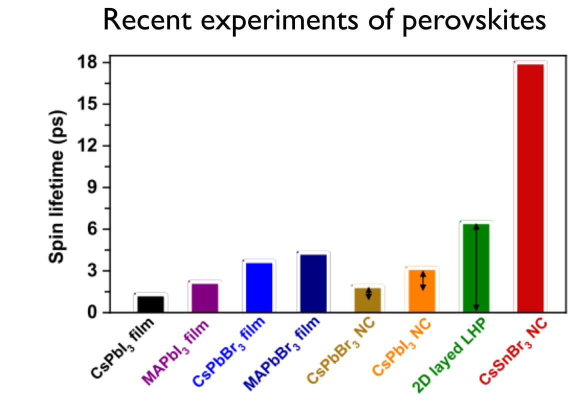
T (K)	n_i (cm^{-2})	τ_p (ps)	$\overline{\mu}_c$ (cm^2/(V s))	D (cm^2/s)	$\tau_{s,z}$ (ns)	$l_{\parallel,s_z}$ (μm)
300	0	0.4	3.2×10^4	830	0.1	2.9
300	1×10^{11}	0.3	2.5×10^4	620	0.1	2.5
50	0	7.2	3.8×10^6	16700	97	400
50	1×10^{11}	1.6	4.5×10^5	2000	76	120
50	1×10^{12}	0.2	5.8×10^4	250	26	25

Spin Relaxation in Lead Halide Perovskites

Perovskite spintronics recently attract strong interests

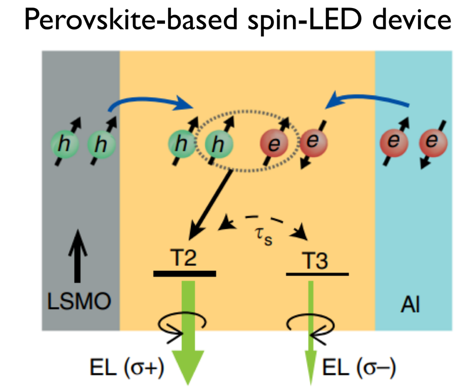


Recent experiments of perovskites



Liang et al., ACS Energy Lett. 6, 1670 (2021)

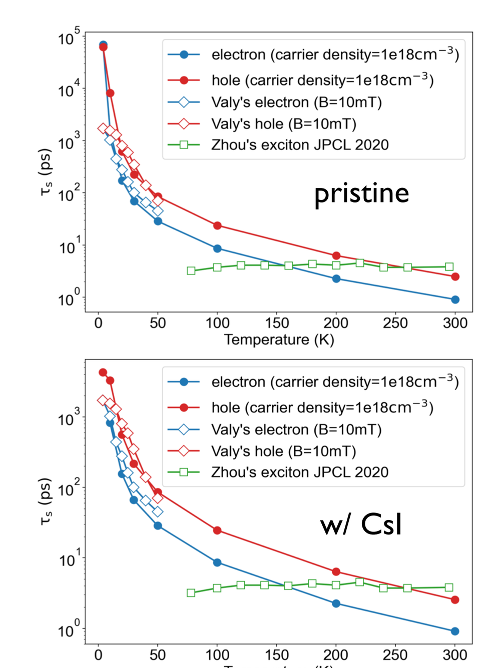
Perovskite-based spin-LED device



Wang et al., Nat. Commun. 10, 129 (2019)

Temperature dependence of τ_s of $CsPbBr_3$

- ❑ Impurities reduce the spin lifetime by more than one order when T < 10 K
- ❑ Theoretical results are in good agreement with the experiments from 4 K to 300 K



(Valy's: Huynh et al. Nat. Commun., 13, 1428 (2022)
(Zhou's: Zhou et al., J. Phys. Chem. Lett. 11, 1502, (2020)

Effects of perpendicular B field

A relatively weak magnetic field B will introduce additional term in Hamiltonian

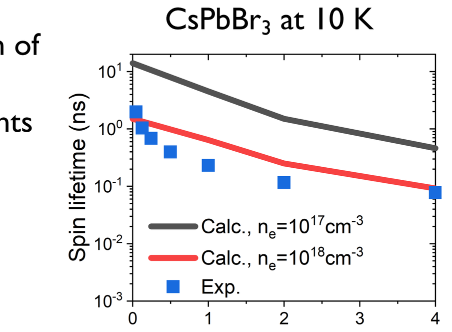
$$H_k(\mathbf{B}) = \mu_B\mathbf{B}\cdot(\mathbf{L}_k + g_0\mathbf{S}_k) \sim \mu_B\mathbf{B}\boldsymbol{g}\cdot\mathbf{S}_k$$

$\mathbf{L} = \frac{1}{2\hbar}(\mathbf{r}\times\mathbf{p} - \mathbf{p}\times\mathbf{r})$ is orbital angular momentum

$\mathbf{B}\boldsymbol{g}$ is understood as an effective total field

The fluctuation of $\mathbf{B}\boldsymbol{g}$ across different k points will induce additional spin relaxation and reduce spin lifetime

CsPbBr3 at 10 K



J. Xu, K. Li, Y. Ping, under preparation (2022)

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