4.2 WSe_2 monolayer

5 Conclusions

Acknowledgments

C.A. and E.C. acknowledge B. Demoulin and A. Saul for the management of the computer cluster *Rosa*. ADD Acknowledgments project COLIBRI and ERASMUS-PLUS.

A Approximated electron-hole interaction

In order to include excitonic effects in the real-time dynamics we derive a simplified screened exchange term. We start from the Appendix of Ref. [28]:

The KBE involves the matrix elements $\langle m,\mathbf{k}|\mathbf{\Sigma^{sex}}|\mathbf{m}',\mathbf{k}\rangle$:

$$\Sigma^{\mathrm{sex}}_{m,m',\mathbf{k}}(t) = i \sum_{\substack{\mathbf{G},\mathbf{G}',\mathbf{q}\\ n,n'}} \rho_{\substack{m,n\\ \mathbf{k},\mathbf{q}}}(\mathbf{G}')\rho^*_{\substack{m',n'\\ \mathbf{k},\mathbf{q}}}(\mathbf{G}) W_{\mathbf{G},\mathbf{G}'}(\mathbf{q})\Delta\gamma_{\substack{n,n'\\ \mathbf{k}-\mathbf{q}}}(t), \tag{11}$$

where $\Delta\gamma$ is the variation of the density matrix, and ρ are the oscillators, defined as:

$$\rho_{\substack{m,n\\ \mathbf{k},\mathbf{q}}}(\mathbf{G}) = \int \varphi^*_{m,\mathbf{k}}(\mathbf{r})\varphi_{n,\mathbf{k}-\mathbf{q}}(\mathbf{r})e^{i(\mathbf{G}+\mathbf{q})\mathbf{r}}. \tag{12}$$

We consider only the long range part of the screened interaction $W(\mathbf{q}) = W_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q})$ and the previous formula reduces to:

$$\Sigma^{\mathrm{lsex}}_{m,m',\mathbf{k}}(t) = i \sum_{\mathbf{q},n,n'} \rho_{\substack{m,n\\ \mathbf{k},\mathbf{q}}}\rho^*_{\substack{m',n'\\ \mathbf{k},\mathbf{q}}} W(\mathbf{q})\Delta\gamma_{\substack{n,n'\\ \mathbf{k}-\mathbf{q}}}(t). \tag{13}$$

The formula above can be rewritten in terms of time-dependent valence bands, by notice that the density matrix is expanded as:

$$\Delta\gamma_{n,m,\mathbf{k}}(t) = \sum_{l=1}^{N_v}\langle u_m|v_{l\mathbf{k}}\rangle\langle v_{l\mathbf{k}}|u_n\rangle - \delta_{n,m}f(\epsilon_{n,\mathbf{k}}) \tag{14}$$

where l is an index on valence bands while n, n', m, m' are indexes on all bands, and $f(\epsilon_{n,\mathbf{k}})$ are the Fermi function. We can rewrite the LSEX self-energy as:

$$\Sigma^{\mathrm{lsex}}_{m,m',\mathbf{k}} = i \sum_{\mathbf{q},l,n,n'} \rho_{\substack{m,n\\ \mathbf{k},\mathbf{q}}}\rho^*_{\substack{m',n'\\ \mathbf{k},\mathbf{q}}} W(\mathbf{q})\langle u_{n'}|v_{l\mathbf{k}\text{-}\mathbf{q}}\rangle\langle v_{l\mathbf{k}\text{-}\mathbf{q}}|u_n\rangle - \Sigma^{eq.}_{m,m',\mathbf{k}}. \tag{15}$$

where Σ^{eq} is the self-energy at equilibrium, defined as:

$$\Sigma^{eq.}_{m,m',\mathbf{k}} = i\sum_{\mathbf{q},n} \rho_{\substack{m,n\\ \mathbf{k},\mathbf{q}}}\rho^*_{\substack{m',n\\ \mathbf{k},\mathbf{q}}} W(\mathbf{q})f(\epsilon_{n,\mathbf{k}-\mathbf{q}}) \tag{16}$$

We then define the oscillators between time-dependent valence bands and Kohn-Sham states as:

$$\tilde{\rho}_{\substack{m,l\\ \mathbf{k},\mathbf{q}}} = \sum_n \rho_{\substack{m,n\\ \mathbf{k},\mathbf{q}}}\langle v_{l\mathbf{k}\text{-}\mathbf{q}}|u_n\rangle \tag{17}$$

and the previous formula reduces to:

$$\Sigma^{\text{lsex}}_{m,m',\mathbf{k}} = i \sum_{\mathbf{q},l} \tilde{\rho}_{\substack{m,l\\ \mathbf{k},\mathbf{q}}} W(\mathbf{q}) \tilde{\rho}^{*}_{\substack{m',l\\ \mathbf{k},\mathbf{q}}} - \Sigma^{eq}_{m,m',\mathbf{k}} \tag{18}$$

To be consistend with this approximation we excluded the local field effects in the dynamics. This approch is similar to the one used in simple models, with the difference that we calculate explicitelly the matrix elements of the Coulomb interaction between the different bands at finite $\mathbf{q}$.

References

[1] K. Khoo, S. G. Louie *et al.*, *Tuning the electronic properties of boron nitride nanotubes with transverse electric fields: A giant dc stark effect*, Physical Review B **69**(20), 201401 (2004).

[2] N. Leisgang, S. Shree, I. Paradisanos, L. Sponfeldner, C. Robert, D. Lagarde, A. Balocchi, K. Watanabe, T. Taniguchi, X. Marie *et al.*, *Giant stark splitting of an exciton in bilayer mos2*, Nature Nanotechnology **15**(11), 901 (2020).

[3] D. Vella, D. Ovchinnikov, N. Martino, V. Vega-Mayoral, D. Dumcenco, Y.-C. Kung, M.-R. Antognazza, A. Kis, G. Lanzani, D. Mihailovic *et al.*, *Unconventional electroabsorption in monolayer mos2*, 2D Materials **4**(2), 021005 (2017).

[4] C. Attaccalite, L. Wirtz, A. Marini and A. Rubio, *Efficient gate-tunable light-emitting device made of defective boron nitride nanotubes: from ultraviolet to the visible*, Scientific Reports **3**(1), 2698 (2013).

[5] Y. Li, Y. Rao, K. F. Mak, Y. You, S. Wang, C. R. Dean and T. F. Heinz, *Probing symmetry properties of few-layer mos2 and h-bn by optical second-harmonic generation*, Nano Letters **13**(7), 3329 (2013), doi:10.1021/nl401561r, `https://doi.org/10.1021/nl401561r`.

[6] X. Yin, Z. Ye, D. A. Chenet, Y. Ye, K. O'Brien, J. C. Hone and X. Zhang, *Edge nonlinear optics on a mos¡sub¿2¡/sub¿ atomic monolayer*, Science **344**(6183), 488 (2014), doi:10.1126/science.1250564, `https://www.science.org/doi/pdf/10.1126/science.1250564`.

[7] J. Klein, J. Wierzbowski, A. Steinhoff, M. Florian, M. Rosner, F. Heimbach, K. Muller, F. Jahnke, T. O. Wehling, J. J. Finley *et al.*, *Electric-field switchable second-harmonic generation in bilayer* mos_2 *by inversion symmetry breaking*, Nano letters **17**(1), 392 (2017).

[8] S. Shree, D. Lagarde, L. Lombez, C. Robert, A. Balocchi, K. Watanabe, T. Taniguchi, X. Marie, I. C. Gerber, M. M. Glazov *et al.*, *Interlayer exciton mediated second harmonic generation in bilayer mos2*, Nature Communications **12**(1), 6894 (2021).

[9] J. Wang, N. Han, Z.-D. Luo, M. Zhang, X. Chen, Y. Liu, Y. Hao, J. Zhao and X. Gan, *Electrically tunable second harmonic generation in atomically thin res2*, ACS nano **16**(4), 6404 (2022).

[10] K. L. Seyler, J. R. Schaibley, P. Gong, P. Rivera, A. M. Jones, S. Wu, J. Yan, D. G. Mandrus, W. Yao and X. Xu, *Electrical control of second-harmonic generation in a wse2 monolayer transistor*, Nature nanotechnology **10**(5), 407 (2015).