Theoretical developments and applications in excited-state calculations

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Nature of Plasmon Satellites in Photoemission Spectroscopy

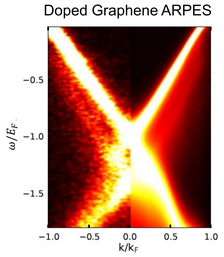
Motivation

- Plasmons and their interactions with electrons and holes are of increasing interest for technological applications, such as plasmonics and catalysis.
- **Goal**: Understand the nature of plasmon satellites that appear in the angle-resolved photoemission spectroscopy (ARPES) measurements on doped graphene and bulk Si.

Doped Graphene

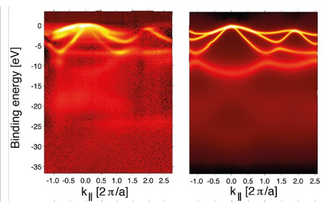
- Previous GW calculations based on simplified models of electron systems, such as the linear-bands model for graphene and the electron gas, predicted the existence of a composite particle, the *plasmaron,* consisting of a hole and a plasmon.
- ARPES experiments on doped graphene showing significant plasmon satellites appeared to support this theory.
- *Ab initio* treatment of substrate and the GW plus cumulant expansion (GW+C) of the interacting green's function give ARPES spectra in good agreement with experiment for all momenta measured.
- No plasmaron appears in spectra, only weak plasmon satellites.
- Agreement of previous theoretical work with experiment was due to cancellation of errors in use of GW approximation and overestimation the screening from the substrate.

Doped Graphene ARPES



Bulk Si

- First measurement and calculation of ARPES spectra of bulk Si, including QP and satellite peaks.
- GW+C again gives good agreement with experiment and gives no plasmaron.



Conclusions

- While sufficient for calculating QP properties, the GW approximation is insufficient for satellite properties, for which you need GW+C.
- The plasmaron is an artifact of the GW approximation and does not exist in nature.
- Common model dielectric functions overestimate substrate screening.

Future Works

- Understand electron-plasmon coupling on surfaces for catalytic applications.
- Include extrinsic contribution to GW+C ARPES spectra to improve agreement of QP and satellite peak weights with experiment.

Collaborators

Theory: Derek Vigil-Fowler, Johannes Lischner, and Steven G. Louie

Experiment: Gunnar K. Palsson and Charles S. Fadley

Accurate GW calculations for closed-shell molecules.

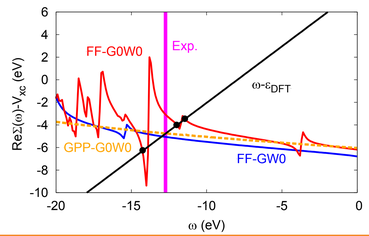
Motivation

- Knowledge of quasiparticle energies of molecules is important for interpreting spectroscopy experiments and the design of novel devices for energy technology, such as Graetzel cells or OLEDs.
- **Goal**: Understanding the effects of self-consistency, full-frequency approaches and generalized plasmon-pole models on quasiparticle energies in closed-shell molecules.

Pitfalls in full-frequency G0W0 calculations

- In molecules, the frequency-dependent electron self energy exhibits poles which describe shake-up excitations consisting of a quasiparticle and an electron-hole pair.
- For molecules with a small HOMO-LUMO gap, the self-energy poles can occur at unphysically low energies inducing large errors in the computed quasiparticle energies.
- Replacing the DFT Kohn-Sham energies by quasiparticle energies within a self-consistent GW0 approach pushes the self-energy poles to higher energies and results in good agreement with experiment.

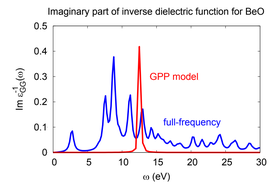
LUMO of ozone



G0W0 calculations with a generalized plasmon-pole model

- The generalized plasmon-pole model replaces the complicated dielectric response of a molecule by a single excitations which must have a high energy to fulfill the f-sum rule.
- As a result, the self-energy poles are shifted to higher energies and accurate quasiparticle energies are obtained.

Imaginary part of inverse dielectric function for BeO



Conclusions

- For molecules with small HOMO-LUMO gaps, full-frequency G0W0 calculations can result in large errors for quasiparticle energies because of unphysical self-energy poles.
- Self-consistent GW0 calculations give good agreement with experiment for quasiparticle energies.
- G0W0 calculations employing a generalized plasmon pole model provide accurate quasiparticle energies at a significantly lower numerical cost than self-consistent full-frequency GW0 calculations.

Future Works

- Understand the effects of full-frequency approaches, self-consistency and the generalized plasmon-pole model on quasiparticle energies in other systems, such as oxide materials.

Collaborators

Theory: Johannes Lischner, Sahar Sharifzadeh, Jack R. Deslippe, Jeffrey R. Neaton and Steven G. Louie.

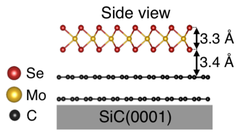
Effect of Substrate Screening on the Quasiparticle and Optical Properties of $MoSe_2$

Motivation

- Transition metal dichalcogenides, such as MoS2 and MoSe2, are interesting candidate materials for electronic and photovoltaic applications.
- **Goal**: Understand the role of substrate used in experiments on the quasiparticle and excitonic properties of MoSe2.

In-Plane Substrate Approximation

- Experimental collaboration: both scanning tunneling spectroscopy and photoluminescense measurements were performed on the same sample.

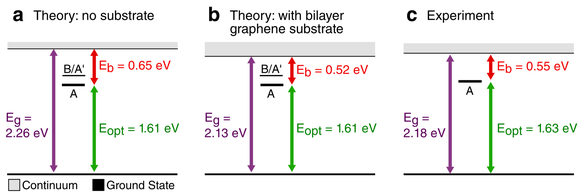


- Challenge: calculate quasiparticle band structure and exciton binding energy of monolayer $MoSe_2$ including the screening from the substrate. The MoSe2 monolayer is only commensurable with the substrate on a 3x3 supercell.
- We developed an *ab initio* method to calculate the screening from the substrate without having to construct a large supercell for the material + substrate.
- Idea: we fully consider the perpendicular component of the screening, but neglect in-plane local fields:

$$\tilde{\chi}^{0,\mathrm{bilayer}}_{\mathbf{GG'}}(\mathbf{q}) = \chi^{0,\mathrm{bilayer}}_{\mathbf{GG'}}(\mathbf{q})\,\delta_{\mathbf{G}_x\mathbf{G}'_x}\delta_{\mathbf{G}_y\mathbf{G}'_y}$$

$$\Delta\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q}) = \left[1 - v\left(\chi^{0,\mathrm{MoSe2}}(\mathbf{q}) + \tilde{\chi}^{0,\mathrm{bilayer}}(\mathbf{q})\right)\right]^{-1}_{\mathbf{GG'}} - \left[1 - v\,\chi^{0,\mathrm{MoSe2}}(\mathbf{q})\right]^{-1}_{\mathbf{GG'}}$$

Effect of the Substrate on Monolayer $MoSe_2$



- Good agreement with experiment when substrate screening is included.

Conclusions

- The In-plane Substrate Approximation is an efficient *ab inito* technique to include the substrate screening.
- For MoSe2 on bilayer graphene substrate, the substrate closes the quasiparticle gap by 130 meV, and decreases the exciton binding energy by a similar amount.

Future Works

- Calculate the effect of metallic screening on $MoSe_2$.
- Apply the method for molecular systems.

Collaborators

Theory: Felipe H. da Jornada, Diana Y. Qiu and Steve G. Louie

Experiment: Feng Wang and Mike F. Crommie groups

Efficiency and Accuracy of PW-PP GW Calculations

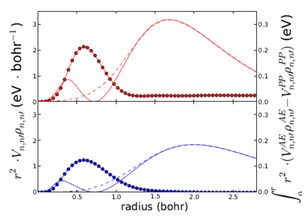
Motivation

- Efficient methods for calculating the QP properties of large systems are needed to adequately treat systems of current interest, including materials with defects and complex materials with large unit cells.
- **Goal**: To understand the effect of the plane-wave pseudopotential (PW-PP) approximation on the accuracy of GW calculations.

Atomic

- Contributions to bare exchange coming from states that have a small (large) separation between outer and inner wavefunction peaks are smaller (larger) for PW-PP GW calculations relative to AE GW calculation.

Si bare exchange density



- Atomic Si, Ga, As, and Ar show small differences in bare exchange between all-electron (AE) and PW-PP GW calculations (~1%).
- Trends are robust across all atoms studied, which vary in localization of electrons and presence of d-states, indicating the trends are robust across different system types.

Bulk

- Wavefunctions in the bulk have larger inner-outer peak separation than in the atomic case due to bonding. The bare exchange is larger for PW-PP GW calculations, as expected from the atomic case.
- The valence band has a larger difference between PW-PP and AE GW calculations than the conduction band, leading to an opening of the gap for PW-PP GW calculations, on the order of 0.1-0.2 eV.
- A cheap correction scheme is to perform a PW-PP calculation for the dynamical self energy and get bare exchange from AE calculation.

Conclusions

- The error due to the PW-PP approximation is small, on the order 0.1-0.2 eV for many standard semiconductors.
- For systems with deep cores, this error can be reduced to ~0.05 eV by calculating only the bare exchange in the AE formalism, with only a minimal loss in computational efficiency. This could be very useful for accurate calculations on large systems.

Future Works

- Investigate efficacy of PAW formalism for shallow-core systems, where computational efficiency is drastically reduced with PW-PP GW.
- Design improved pseudopotentials including accurate exchange integrals as constraint during generation.

Collaborators

Theory: Derek Vigil-Fowler, Brad D. Malone and Steven G. Louie

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