Excitations in Molecules and Nano-Clusters

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Supported by the National Science Foundation under Award Number DMR-03 25939 ITR, via the Materials Computation Center at the University of Illinois at Urbana-Champaign DOE Computational Materials Science Network

Introduction and Motivation

We are studying excitations and optical properties of Hydrogen passivated Ge clusters. Single-body methods such as Density Function Theory in the Local Density Approximation (LDA) underestimate band gaps (Ge is a metal), while Hartree-Fock (HF) overestimates gaps. For this reason we propose to use Quantum Monte Carlo (QMC) which is a many-body method.

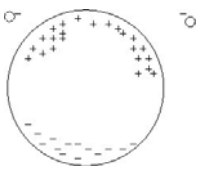
Core-Valence Partitioning for Ge

•Ge has a shallow and easily polarizable 3d core**.**
•Ge nano-crystals require the use of pseudopotentials due to the system size and the scaling properties of QMC with respect to the atomic number *Z*

Core Polarization Potentials (CPPs)

•CPPs include many-body effects within the core partitioning scheme; include in valence Hamiltonian.
•Valence electrons induce a core-polarization and feel the induced potential.

$$V_{CPP} = -\frac{1}{2}\sum_C \alpha_C \mathbf{E}_C \cdot \mathbf{E}_C$$

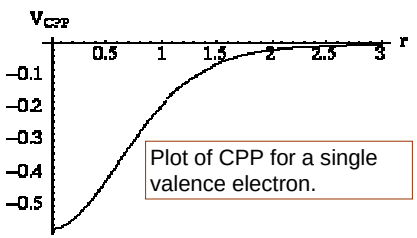


Right) Two valence electrons polarizing a core.

•Electric field which acts on core *C* due to the valence electrons and the other cores.

$$\mathbf{E}_C = \sum_i \frac{\mathbf{r}_{Ci}}{r_{Ci}^3} f(r_{Ci}) - \sum_{C' \neq C} \frac{\mathbf{R}_{CC'}}{\mathbf{R}_{CC'}^3} Z_{C'} = \mathbf{E}_C^e + \mathbf{E}_C^n$$

Where $f(r_{Ci})$ is a cutoff function for the electric field inside the core (E.L Shirley and R.M. Martin: PRB **47**, 15413 (1993)).



Plot of CPP for a single valence electron.

Computational Method and Details

- *qmcPlusPlus*: Object oriented application package to perform QMC [Variational (VMC) and Diffusion (DMC)] developed at the MCC and NCSA using open-source libraries (HDF5 and XML). http://www.mcc.uiuc.edu/qmc/
- HF performed by Gaussian03.
- For Ge: Use a Dirac-Fock pseudopotential (non-local) from the library provided by the group of R. J. Needs with basis (*sp/sp/sp/sp/d*) = *21 Gaussians*

http://www.tcm.phy.cam.ac.uk/~mdt26/pp_lib/ge/pseudo.html

- For H: Use -1/r potential with basis *(s/s/p)* = 6 Gaussians.

QMC Calculations of Optical Properties

- QMC explicitly includes correlation: optical gaps depend on the interaction of the exiton with all the electrons.
- Use Slater-Jastrow trial function:

$$\Psi_T(\mathbf{R}) = \mathbf{e}^{\mathbf{J}(\{\alpha\},\mathbf{R})}\mathbf{D}^{\uparrow}(\mathbf{r}_1,\ldots,\mathbf{r}_{\mathbf{N}_\uparrow})\mathbf{D}^{\downarrow}(\mathbf{r}_{\mathbf{N}_\uparrow+1},\ldots,\mathbf{r}_{\mathbf{N}})$$

- ***D*** is a determinant of single particle orbitals and ***J*** is the Jastrow.
- The optical gap: $E_{gap}^{opt} = -\left(E_{tot}^{gs}[\Psi_T^{gs}] - E_{tot}^{ex}[\Psi_T^{ex}]\right)$

where Ψ_T^{gs} is the ground state and Ψ_T^{ex} is an excited state.

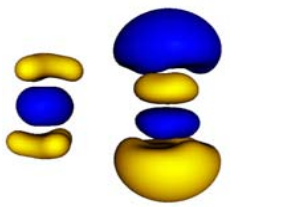
$$D^{\uparrow} = \begin{vmatrix} \psi_1(\mathbf{r}_1) & \ldots & \psi_1(\mathbf{r}_{\mathbf{N}/2}) \\ \vdots & \vdots & \vdots \\ \psi_{N/2}(\mathbf{r}_1) & \ldots & \psi_{N/2}(\mathbf{r}_{\mathbf{N}/2}) \end{vmatrix} \rightarrow \begin{vmatrix} \psi_1(\mathbf{r}_1) & \ldots & \psi_1(\mathbf{r}_{\mathbf{N}/2}) \\ \vdots & \vdots & \vdots \\ \psi_{N/2+1}(\mathbf{r}_1) & \ldots & \psi_{N/2+1}(\mathbf{r}_{\mathbf{N}/2}) \end{vmatrix}$$

For Ψ_T^{ex} replace a HOMO state with a LUMO state in $D^{\uparrow}$.

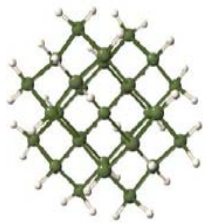
Results for Atomic Removal and Excitation Energies

	$s^2p^2(3P) \longrightarrow sp^2(4P)$	$s^2p^2(3P) \longrightarrow sp^3(5S)$
DMC+CPP	5.1203(18)	14.3737(23)
Expt.	5.1	14.3
VMC+CPP	4.87715(73)	14.24249(98)
DMC	4.7445(16)	13.9442(22)
VMC	4.51420(73)	13.8452(11)
GW	4.3	13.5
HF	3.475288	12.278999

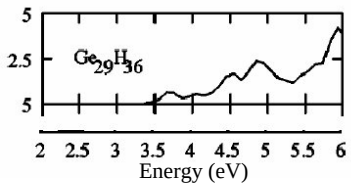
Results for Optical Gaps



Ge_2H_6



$Ge_{29}H_{36}$



Time-Dependant LDA results for Ge29H36 (A.Tsolakidis and R.M.Martin, PRB **71**, 125319 (2005)).

	GeH_4	Ge_2H_6	$Ge_{29}H_{36}$
HF	17.719	15.006	10.267
VMC	10.524(12)	8.185(16)	5.641(71)
$VMC+CPP$	10.266(12)	7.976(18)	5.508(71)
DMC	9.634(14)	7.708(21)	6.02(57)
$DMC+CPP$	9.479(14)	7.541(12)	5.94(57) *

Hartree-Fock and Quantum Monte Carlo optical gaps $\mathbf{E}_{\mathbf{gap}}^{\mathbf{opt}}$ (all energies in eV). *Preliminary result

Conclusions and Future Work

- CPP is an important effect for atomic excitations and at the exitonic level for the optical gap of molecules and clusters.
- CPP can be treated as a perturbation.
- Study more clusters and the effect of CPP on the band gap.

Thanks to Eric L. Shirley and NIST for discussions.