Supplemental material for the paper "Van der Waals Interactions in Ionic and Semiconductor Solids"

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1 Computational Details on the Time-Dependent Density Functional (TDDFT) approaches

1.1 Periodic calculations for the optical spectra

The optical absorption spectra for C, Si, and Ge have been calculated using TDDFT response theory for a series of cell volumes within $\pm 20\,\%$ of the experimental equilibrium volume. Calculations are based on the adiabatic local density approximation (ALDA) and Heyd-Scuseria-Ernzerhof (HSE) exchange-correlation functionals, where the latter includes a fraction of *screened* Hartree-Fock–type exchange[1]. Contributions to the exchange-correlation kernel f_{xc} originating from the nonlocal Fock-type exchange have been calculated following the approach described in Refs. [2-5] [nanoquanta (NQ) kernel]. Results presented in the main article have been obtained by employing the projector augmented plane-wave (PAW) code VASP[6]. The HSE functional used a screening parameter of $0.3\,\text{Å}^{-1}$ and was chosen to best fit experimental absorption spectra.

Discussing technical details for calculations on C, Si, and Ge, only outer valence s and p electrons have been used for the self-consistent field as well as excited state calculations. The respective [He], [Ne], and [Ar]$3d^{10}$ electrons were treated as core and kept frozen in the configuration determined as the PAW core potential was generated using the local density approximation (LDA) or the Perdew-Burke-Ernzerhof[7] (PBE) gradient-corrected density functional. We carefully checked the importance of $3d$ electrons for Ge, and did not find noticeable change in the spectra. For C, Si, and Ge,

the default kinetic energy cutoffs of 414, 245.7, and 173.8 eV have been applied, respectively. Calculations using a 40 % higher cutoff did not change the spectra quality over the entire volume range. Gaussian smearing using a width of 0.05 eV was applied throughout this work. Furthermore, 12 conduction bands were used and we employed "shifted k meshes" as described in Ref. [8] to achieve k-point convergence. TDLDA calculations for C and Si used $32 \times 32 \times 32$ k points, for Ge, due to the smaller gap, we used a mesh of $56 \times 56 \times 56$ k points. TDHSE+NQ calculations for C and Si employ the same mesh as used for TDLDA, but due to the larger computational workload for setting up the nonlocal nanoquanta kernel, $40 \times 40 \times 40$ k points were used for the Ge TDHSE+NQ spectrum.

Concerning results presented for the binary solids, frozen [He] (for oxygen), [Ne] (for Cl, Na, Mg) and $[Ar]3d^{10}$ (for Ga, and As) cores were used. Excited state calculations for NaCl, MgO, and GaAs are again carried out using 12 conduction bands and a $32 \times 32 \times 32$ k-point mesh. The respective plane-wave kinetic energy cutoffs for NaCl, MgO, and GaAs amount to 350, 400, and 210 eV.

Smoothness of the optical spectra and comparison to experiment suggest that results are practically k point converged. For the TDHSE+NQ spectra of Si, C, and GaAs and for more information on the general performance and implementation of TDHSE employing the nanoquanta kernel can be found in Ref. [8].

1.2   Cluster extrapolation (CE) model

The TDDFT cluster calculations were performed for C, Si, and Ge for evaluating the "bulk atom" polarizability and C_6 dispersion coefficients from the cluster polarizability and C_6 coefficients. For silicon cluster, we obtained the geometries from S. Botti[9]; for C and Ge, we built equivalent models on the basis of Si clusters; all the clusters are cut from the bulk and saturated with hydrogen atoms. The volume effects have been studied by changing the distance between (C, Si, and Ge) atoms. For every cluster structure, only the hydrogen atoms were relaxed using the Fritz Haber Institute *ab initio* molecular simulations package[10] (FHI-aims) with the PBE exchange-correlation functional. Using the optimized geometries, we solved the Sternheimer linear-response equations[11], as implemented in the OCTOPUS code[12], with the ALDA parametrization for the xc potential. For a real-space regular grid, the spacing of 0.275 Å is chosen to ensure convergence, and a radius of 4.5 Å is used for constructing the simulation box by adding spheres around each atom. With the above computational settings, the cluster polarizability and C_6 dispersion coefficients were obtained.

TABLE I. Calculated polarizabilities α (in bohr^3) and C_6 dispersion coefficients (in hartree· bohr^6) for C, Si, and Ge bulk at their experimental lattice constants a_0 (in Å) within LDA and HSE functionals. The results derived from the Clausius-Mossotti (CM) equation and cluster extrapolation (CE) model were compared.

| | a_0 | α | | | C_6 | | |
	Expt.	HSE$^{\mathrm{CM}}$	LDA$^{\mathrm{CM}}$	LDA$^{\mathrm{CE}}$	HSE$^{\mathrm{CM}}$	LDA$^{\mathrm{CM}}$	LDA$^{\mathrm{CE}}$
C	3.567	5.5	5.7	5.0	16.7	16.8	17.2
Si	5.430	25.0	25.9	26.0	166.0	171.9	176.6
Ge	5.652	30.3	32.1	31.1	224.5	231.9	238.3

TABLE II. The atomic parameters for the vdW correction of six solids at their experimental lattice constants: polarizabilities α (in bohr^3), vdW radii R_{vdW} (in bohr), and C_6 coefficients (in hartree· bohr^6). Free atom values are given with superscript or subscript of "free".

	α_{solid}	α_{free}	$R_{\mathrm{vdW}}^{\mathrm{solid}}$	$R_{\mathrm{vdW}}^{\mathrm{free}}$	C_6^{solid}	C_6^{free}
C	5.5	12	2.77	3.59	16.7	46.6
Si	25.0	37	3.68	4.2	166	305
Ge	30.3	41	3.8	4.2	224.5	354
Mg	9.2	71	2.16	4.27	38.6	627
O	2.2	5.4	2.36	3.19	2.2	15.6
Ga	29.1	60	3.29	4.19	213	498
As	26.7	29	4	4.11	179	246
Na	13.6	162.7	1.63	3.73	69.3	1556
Cl	8	15	3	3.71	23.7	94.6

2 Experimental and calculated cohesive properties

TABLE III. Experimental values of lattice constants a_0 (in Å), bulk moduli B_0 (in GPa), pressure derivative of bulk modulus B', and cohesive energies E_{coh} (in eV/atom). Experimental data is from Refs. 13 and 14 unless otherwise stated.

	a_0	B_0	B'	E_{coh}
C	3.567	443	4.0[a]	-7.37
Si	5.430	99	4.2[b]	-4.62
Ge	5.652	76	3.0[c]	-3.87
GaAs	5.648	76	4.7[d]	-3.31
NaCl	5.595	28[e]	4.9[e]	-3.31
MgO	4.207	169[f]	4.1[g]	-5.12

[a] Reference 15
[b] Reference 16
[c] Reference 17
[d] Reference 18
[e] Reference 19
[f] Reference 20
[g] Reference 21

TABLE IV. Calculated cohesive properties for C, Si, and Ge crystals. The quasiharmonic zero-point energy is calculated using the phonon spectrum for every functional, except HSE06, where the PBE phonon spectrum is used.

TABLE V. Calculated cohesive properties for binary GaAs, NaCl, and MgO crystals.

		a_0 (Å)	E_{coh} (eV/atom)	B_0 (GPa)	$B^{'}$
C	LDA	3.546	-8.76	457	3.6
	PBEsol	3.568	-8.10	440	3.7
	PBE	3.585	-7.55	423	3.8
	HSE06	3.561	-7.43	456	3.6
	PBE+vdW	3.576	-7.74	429	3.7
	HSE06+vdW	3.554	-7.60	464	3.7
	Expt.	3.567	-7.37	443	4.0
Si	LDA	5.412	-5.23	96	4.4
	PBEsol	5.443	-4.88	93	4.4
	PBE	5.481	-4.49	88	4.2
	HSE06	5.444	-4.52	97	3.8
	PBE+vdW	5.459	-4.77	91	4.2
	HSE06+vdW	5.425	-4.78	100	3.7
	Expt.	5.430	-4.62	99	4.2
Ge	LDA	5.630	-4.54	69	5.0
	PBEsol	5.681	-4.11	65	5.0
	PBE	5.770	-3.69	56	5.1
	HSE06	5.691	-3.68	71	4.8
	PBE+vdW	5.718	-3.98	73	3.1
	HSE06+vdW	5.653	-3.96	84	3.6
	Expt.	5.652	-3.87	76	3.0

		a_0 (Å)	E_{coh} (eV/atom)	B_0 (GPa)	B'
MgO	PBE	4.271	-4.91	145	4.1
	HSE06	4.223	-4.83	161	4.5
	PBE+vdW	4.241	-5.09	160	4.2
	HSE06+vdW	4.203	-5.00	177	4.5
	Expt.	4.207	-5.12	169	4.1
GaAs	PBE	5.755	-3.12	59	5.0
	HSE06	5.693	-3.12	71	4.6
	PBE+vdW	5.669	-3.39	71	5.5
	HSE06+vdW	5.631	-3.39	83	5.0
	Expt.	5.648	-3.31	76	4.7
NaCl	PBE	5.723	-3.07	23	4.6
	HSE06	5.689	-3.07	23	4.9
	PBE+vdW	5.562	-3.27	30	4.9
	HSE06+vdW	5.543	-3.27	32	4.7
	Expt.	5.595	-3.31	28	4.9

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