Supporting Information

Electronic, optical, and elastic properties of CaFI monolayer and acoustic phonon dispersion at hypersonic frequencies using density functional theory and beyond with random phase approximation and Bethe-Salpeter equation

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The response function is:

\[
\chi^0(r, r', i\omega) = \sum_{ij} \frac{(f_i - f_j)\psi^*_i(r)\psi_j(r)\psi^*_j(r')\psi_i(r')}{\epsilon_i - \epsilon_j - i\omega}.
\] (1)

The other strategy in eliminating self-interaction failure is to employ a way beyond DFT, for example, the GW approach. The pseudonym 'GW' develops from the numerical formulation of the puzzle where G is the Green function G. While W is the screened Coulomb interaction and \(\epsilon\) is energy; combining over the output GW provides the XC interaction. The relation between the function of Green without interaction G and the function of Green of a system in interaction G is given by the equation of Dyson:

\[
G^{-1}(x, x', \omega) = G^{-1}_H(x, x', \omega) - \Sigma(x, x', \omega),
\] (2)

Where the self energy \(\Sigma\) includes multiple body effects due to exchange and correlation. The poles of the interacting Green function can be found by solving the equation of quasi particle (QP):

\[
H_0(x)\psi^{QP}_n(x) + \int dxt\Sigma(x, x', E^{QP}_n)\psi^{QP}_n(x') = E^{QP}_n\psi^{QP}_n(x),
\] (3)

the QP energies are complex quantities describing the position \((ReE^{QP}_n)\) and the width \((ImE^{QP}_n)\) of the QP peaks. The relation between the function of Green G, the self energy \(\Sigma\), the irreducible polarizability P, the Coulomb filtered interaction \(W = \epsilon^{-1}\nu\), and the so-called vertex function \(\Gamma\) is given by Hedin’s equations \([(x_i, t_i) =: i]:

\[
P(12) = -i\int d(34)G(13)G(41^+)\Gamma(342).
\] (4)

\[
W(12) = \nu(12) + \int d(34)W(13)P(34)\nu(42).
\] (5)

\[
\Sigma(12) = i\int d(34)G(14^+)W(13)\Gamma(423).
\] (6)
\[ \Gamma(123) = \delta(12)\delta(13) + \int d(4567) \frac{\delta \Sigma(12)}{\delta \Sigma G(45)} \times G(46)G(75)\Gamma(673). \] (7)

\[ G(12) = G_{KS}(12) + \int d(34)G_{KS}(13)\Sigma(34)G(42). \] (8)

\[ \Sigma(12) = iG(12^+)W(12). \] (9)

The equation 9 is explaining the name of the approximation "GW". The element’s QP energies are derived from a perturbative evolution of the electron self-energies and the dielectric function in this method.

For the SOECs and TOECs: we consider \( a_i \) as the fundamental coordinates of the material element. The coordinates obtained after application of a homogeneous elastic deformation are \( x'_i = x(a_j) \). The deformation is represented by the deformation gradient:

\[ F_{ij} = \frac{\partial x_i}{\partial a_j}. \] (10)

The finite Lagrangian strains is explained by:

\[ \eta_{ij} = \frac{1}{2} \sum_k (F_{ki}F_{kj} - \delta_{ij}). \] (11)

With a collection of pleasantly taken strain tensors for tetragonal systems, we can calculate the elastic constants from the Lagrangian strains. These constants are established by extending the internal energy per unit mass \( U \) as a Taylor series in the strain at constant entropy: \(^{1-3}\)

\[ \rho_0 U(\eta_{ij}, S) = \rho_0 U(0, S) + \frac{1}{2} \sum_{ijkl} C_{ijkl}^s \eta_{ij} \eta_{kl} + \frac{1}{6} \sum_{ijklmn} \sum_{ijkl} C_{ijklmn}^s \eta_{ij} \eta_{kl} \eta_{mn} + \ldots \] (12)

\( \rho_0 \) is the mass density. The expansion coefficients of the Taylor series in equation 12 are the
isentropic elastic constants.\(^{1-3}\)

\[
\sum_{ijkl} C^s_{ijkl} = \rho_0 \frac{\partial^2 U}{\partial \eta_{ij} \eta_{kl}} |_{\eta=0} (SOEC),
\]

\[
\sum_{ijklmn} C^s_{ijkl} = \rho_0 \frac{\partial^3 U}{\partial \eta_{ij} \eta_{kl} \eta_{mn}} |_{\eta=0} (TOEC),
\]

the relationship between SOECs \(C^s_{ijkl}\), TOECs \(C^s_{ijklmn}\) and energy total per mass is determined by:

\[
\rho_0 [U(\xi) - U(0)] = \frac{1}{2} A_2 \xi^2 + \frac{1}{6} A_3 \xi^3 + O(\xi^4).
\]

Where \(U(0)\) is the energy for the initial state and \(\xi\) is the magnitude levels. The coefficients \(A_2\) and \(A_3\) are alliances of second-and third-order elastic constants, respectively. For strain parameter \(\xi\), we employ the range \(-0.025 \leq \xi \leq 0.025\) with a strain step size of \(\Delta \xi = 0.0025\). Then, we have applied the elastic constants, in particular, SOECs to distinguish the mechanical properties such as bulk modulus (B), shear modulus (G), Young’s modulus (E), and Poisson’s ratio coefficients (\(\nu\)). They were determined as Voigt-Reuss-Hill averages (VRH).\(^4\) Note that the properties of stable compounds to disfigure below the applicability of an external force and to retrieve their initial form after the force is eliminated is related to its elasticity. The external force employed on a particularized field is identified as stress, while the quantity of deformation is named the strain. We describe the bulk modulus \((B_{VRH})\) and shear modulus \((G_{VRH})\) in equation 16.

\[
B_{VRH} = \frac{(B_V + B_R)}{2}.
\]

\(B_V\) and \(B_R\) are the bulk Voigt-Reuss, respectively. They are defined by:

\[
B_V = \frac{1}{9} [2(C_{11} + C_{12}) + C_{33} + 4C_{13}].
\]
\[ B_R = \frac{C^2}{M}. \]  

(18)

\[ M = (C_{11} + C_{12}) + 2C_{33} - 4C_{13}. \]  

(19)

\[ C^2 = \frac{(C_{11} + C_{12})}{C_{33} - 2C_{13}^2}. \]  

(20)

Shear modulus is described this way:

\[ G_{VRH} = \frac{(G_V + G_R)}{2}. \]  

(21)

Shear Voigt is represented by \( G_V \) and is associated to SOECs:

\[ G_V = \frac{1}{30}[M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66}]. \]  

(22)

From the elastic constants, we could also construct shear Reuss:

\[ G_R = \frac{15}{18B_V} + \frac{6}{(C_{11} - C_{12})} + \frac{6}{C_{44}} + \frac{3}{C_{66}}. \]  

(23)

The material’s Young’s modulus \( E_{VRH} \) is an essential property in physical design process. It is regarded by:

\[ E_{VRH} = E_H = \frac{9G_{VRH}B_{VRH}}{G_{VRH} + 3B_{VRH}}. \]  

(24)

Also, the interrelations between Poisson’s ratio \( (\nu_{VRH}) \) and the others moduli for solids are as follows:

\[ \nu_{VRH} = \nu_H = \frac{3B_{VRH} - 2G_{VRH}}{6E_{VRH} + 2G_{VRH}} = \frac{E_{VRH}}{2G_{VRH}} - 1. \]  

(25)

Universal anisotropy index is defined by:

\[ A^U = \frac{5G_V}{G_R} + \frac{B_V}{B_R} - 6. \]  

(26)

For isotropic crystal \( A^U = 0 \) and deviations of \( A^U \) from zero define the extent of elastic
anisotropy (EA). $A_B$ elastic anisotropy in compressibility:

$$A_B = \frac{B_V - B_R}{B_V + B_R}. \quad (27)$$

Also, the elastic anisotropy in shear is determined by:

$$A_G = \frac{G_V - G_R}{G_V + G_R}. \quad (28)$$

The deformation gradient $F_{ij}$ was applied to the crystal lattice vectors $r$ of the unit cell for the strained crystal to determine the unstrained lattice vectors $r_i$ and to compute the total energy. Besides, note that our system is tetragonal, therefore:

$$C_{11} > 0, C_{33} > 0, C_{44} > 0, C_{66} > 0. \quad (29)$$

Besides,

$$(C_{11} - C_{12}) > 0, (C_{11} + C_{33} - 2C_{13}) > 0, 2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0. \quad (30)$$

The magnitude of the wave vector $q$ of an acoustic mode is defined by:

$$q = 2(\eta^2 + \kappa^2)^{1/2}k. \quad (31)$$

$k = 2\pi/\lambda$, $\lambda$ is a wavelength, and $(\eta + i\kappa)$ is the medium’s complex refractive index. The frequency of the phonon mode, with the spectral line form defined by:

$$\nu = \frac{Vk}{\pi(\eta^2 + \kappa^2)^{1/2}} = \frac{Vq}{2\pi}. \quad (32)$$

$V$ is the phonon velocity:

$$\nu = F \times q + b. \quad (33)$$
Note that the disparity between a N electron structure’s ionization energy and electron attraction is defined as the meaningful energy band gap:

\[ E_{\text{gap}}(N) = I(N) - A(N) = E(N + 1) + E(N - 1) - 2E(N) \]  \hspace{1cm} (34)

\[ E_{\text{gap}}(N) = \int_0^1 \left( \frac{\partial E}{\partial N} \right)_{N+1}^{N-1+f} df. \]  \hspace{1cm} (35)

Hereabouts \( E(N) \) represents the N electron system’s ground state energy, and \( f \) denotes a percent of an electron. The optical gap, also known as the system’s first electronic excited state, is a related term. The effects of relaxation result in optical gaps that are less than substantial gaps. Nonetheless, in semiconductors, the two are frequently confused. The partial derivatives in equation 35 can be expressed in terms of the exact highest-occupied Kohn-Sham eigenvalues using Janak’s theorem:

\[ E_{\text{gap}}(N) = \int_0^1 \left( \epsilon_{N+1}^{KS}(N + f) - \epsilon_N^{KS}(N - 1 + f) \right) df, \]  \hspace{1cm} (36)

\( \epsilon_i(N) \) is the \( i \)th KS orbital energy for an N electron system. In terms of the number of electrons, the actual Kohn-Sham energy is piece-wise linear.

\[ E_{\text{gap}}(N) = \lim_{f \to 0} [\epsilon(N + f)^{KS} - \epsilon_N^{KS}(N - f)]. \]  \hspace{1cm} (37)

Redrafting equation 37 in words of quantities received from the N-electron system provides:

\[ E_{\text{gap}}(N) = E_{\text{gap}}^{KS}(N) + \Delta_{XC}(N). \]  \hspace{1cm} (38)

\[ E_{\text{gap}}^{KS} = \epsilon_{N+1}^{KS}(N) - \epsilon_N^{KS}. \]  \hspace{1cm} (39)

The derivative discontinuity \( \Delta_{XC}(N) \) results from a discontinuous shift in \( v_{XC}(r) \) as the
electron number passes through integer values.

\[ \Delta_{XC}(N) = \epsilon_{N+1}^{KS}(N + f) - \epsilon_{N}^{fS}. \]

(40)

**GGA-Data about geometry structure of CaFI**

audit creation method 'vasp2cif/FINDSYM'
symmetry space group name H-M "P 4/n 21/m 2/m (origin choice 2)"
symmetry Int Tables number 129
cell length a 3.9400000
cell length b 3.9400000
cell length c 17.00000

cell angle alpha 90.00000

cell angle beta 90.00000

cell angle gamma 90.00000

loop

space group symop id

space group symop operation xyz

1 x,y,z

2 x+1/2,-y,-z

3 -x,y+1/2,-z

4 -x+1/2,-y+1/2,z

5 -y,-x,-z

6 -y+1/2,x,z

7 y,-x+1/2,z

8 y+1/2,x+1/2,-z

9 -x,-y,-z

10 -x+1/2,y,z
11 x,-y+1/2,z
12 x+1/2,y+1/2,-z
13 y,x,z
14 y+1/2,-x,-z
15 -y,x+1/2,-z
16 -y+1/2,-x+1/2,z

loop

atom site label
atom site type symbol
atom site symmetry multiplicity
atom site Wyckoff label
atom site fract x
atom site fract y
atom site fract z
atom site occupancy

I1 I 2 c 0.25000 0.25000 0.88679 1.00000
Ca1 Ca 2 c 0.25000 0.25000 0.04908 1.00000
F1 F 2 a 0.75000 0.25000 0.00000 1.00000

References

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