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Excitons are electron-hole pairs appearing below the band gap in insulators and semiconductors. They are vital to photovoltaics, but are hard to obtain with time-dependent density-functional theory (TDDFT), since most standard exchange-correlation (xc) functionals lack the proper long-range behavior. Furthermore, optical spectra of bulk solids calculated with TDDFT often lack the required resolution to distinguish discrete, weakly bound excitons from the continuum. We adapt the Casida equation formalism for molecular excitations to periodic solids, which allows us to obtain exciton binding energies directly. We calculate exciton binding energies for both small- and large-gap semiconductors and insulators, study the recently proposed bootstrap xc kernel [S. Sharma *et al.*, Phys. Rev. Lett. **107**, 186401 (2011)], and extend the formalism to triplet excitons.

I. INTRODUCTION

Excitons arise from electron-hole attraction in gapped periodic systems such as bulk insulators and semiconductors, as well as in many types of nanoscale systems, polymers and biomolecules.[1,2] Bound excitons appear in optical spectra of extended systems as discrete absorption peaks below the quasiparticle gap, while continuum excitons enhance the band-edge absorption.[3] Excitons play an important role in photovoltaics, where photo-excited excitons propagate to heterojunctions and dissociate to yield currents. Although the phenomenological Wannier model[3–5] describes excitons qualitatively well, it is not quantitatively suitable to be used in real applications where *ab initio* computation is required.

The most important characteristic of bound excitons is their binding energy, defined as the difference between the quasiparticle gap and the excitation frequency of the exciton. The Bethe-Salpeter equation (BSE), a many-body method, is the standard way of calculating exciton binding energies in periodic systems,[6] due to its accuracy. However, the scaling of the computational cost for BSE versus system size is not favorable, and the use of the BSE has therefore been limited to moderate system sizes, despite recent progress.[7–10]

Thanks to the balance of accuracy and computational cost, density-functional theory (DFT) and time-dependent density-functional theory (TDDFT) are popular *ab initio* methods for electronic structure and dynamics.[11,12] Instead of approaching the many-body problem directly, density-functional methods construct a noninteracting Kohn-Sham system with the same electronic density as the original interacting system, which is much easier to solve than the original many-body problem. Despite some additional difficulties for periodic systems (in particular, the severely underestimated gap), TDDFT methods are gaining popularity in solid-state physics.[6,13,14]

TDDFT is a formally exact theory for electron dynamics, but in practice the exchange-correlation (xc) kernel must be approximated. It has been notoriously difficult to get excitons in TDDFT:[15–19] local and semilocal xc kernels that work well in finite systems do not yield bound excitons in solids, since they lack a long-range part.[20] The recently proposed long-range correction (LRC) xc kernel[20–22] allows bound excitons to be obtained from TDDFT, but empirical input is required.

Aside from the difficulty to find good xc kernels, there is another problem. TDDFT approaches for periodic systems typically calculate the optical spectrum via the dielectric function; but exciton binding energies in semiconductors are usually in the meV range, which means that bound excitons require a high frequency resolution to be distinguished from the continuum. This makes the calculation numerically demanding. One could increase the frequency resolution near the region of interest, but this requires knowing the exciton binding energies beforehand. As a consequence, most existing TDDFT studies of excitons are either for materials with strongly bound excitons far away from the band edge such as LiF or Ar,[23] or describe the enhancement of the band-edge continuum spectrum due to excitonic effects.[6,13]

We recently proposed an alternative TDDFT approach for obtaining excitonic binding energies directly.[24–26] The approach was applied to one-dimensional model systems,[26] where we showed that TDDFT within the adiabatic approximation can yield more than one exciton if local-field effects are included. We also considered several bulk solids and found that TDDFT, using xc kernels with appropriate long-range behavior, can yield excitonic binding energies in the right range.[25] However, this earlier work remained somewhat inconclusive due to several simplifications (most notably, a two-band approximation, a rather small k-space grid, and a real-space representation of the xc kernel which resulted in a loss of accuracy).

In this paper we present a systematic computational study of the lowest excitonic binding energies in common zincblende and wurtzite semiconductors as well as in large-gap insulators. We extend our earlier work[25] in several ways: we go beyond the two-band approxima-

tion and include, in principle, an arbitrary number of bands; this can be viewed as the solid-state analog of the Casida approach for molecular excitation energies.[27] Furthermore, we extend the formalism to include triplet excitons, and we test the so-called bootstrap xc kernel.[28]

Atomic units ($e = \hbar = m_e = 1/(4\pi\epsilon_0) = 1$) are used throughout this paper unless mentioned otherwise.

II. THEORETICAL BACKGROUND

In semiconductors, the binding between an electron and a hole is usually weak: such electron-hole pairs are designated as Wannier excitons. The Wannier model[3–5] describes such excitons in analogy to positronium, where the effect of the material environment is introduced by the effective mass and the dielectric constant. The Wannier equation for excitons is given by

$$\left[-\frac{\nabla^2}{2m_r} - \frac{1}{\epsilon r}\right] \psi_\nu(\mathbf{r}) = E_\nu \psi_\nu(\mathbf{r}), \quad (1)$$

where $m_r = (m_h^{-1} - m_e^{-1})^{-1}$ is the reduced effective mass, ϵ is the dielectric constant of the material, and E_ν and ψ_ν are excitonic binding energy and wave function, respectively. The binding energy is the most important property for excitons, defined as the difference between the quasiparticle gap and the excitonic excitation energy. Despite the simplicity of Eq. (1), its exciton binding energies can be fairly accurate for common semiconductors such as GaAs[29] and Cu$_2$O,[30] since the model can be derived as an approximation to the BSE many-body theory[31] (assuming the effective Bohr radii of excitons are much greater than the lattice constant).

Excitons in large-gap materials (such as LiF and Ar) are strongly bound and localized within a single crystal unit. The Bohr radii of these so-called Frenkel excitons are small, so the Wannier model does not describe Frenkel excitons well. However, from the point of view of an *ab initio* electronic structure theory, there is no conceptual difference between Wannier and Frenkel excitons, as they all are just excitations of the many-body system. The collective character of the excitons distinguishes them from other excitations, i.e., they arise from superpositions of many single-particle excitations.

Aside from their collective quasiparticle character, excitons are normal optical excitations. TDDFT has been successful in treating excitations in finite systems, and its use for periodic systems is increasing. TDDFT solves a non-interacting time-dependent system described by the time-dependent Kohn-Sham equation:

$$i\frac{\partial}{\partial t}\phi(\mathbf{r}, t) = \left[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}, t) + v_{\text{H}}(\mathbf{r}, t)\right. $$
$$\left. + v_{\text{xc}}(\mathbf{r}, t)\right]\phi(\mathbf{r}, t), \quad (2)$$

where v_{ext} and v_{H} are the external potential and the Hartree potential, respectively, v_{xc} is the exchange-correlation (xc) potential, and ϕ is a time-dependent

Kohn-Sham orbital. v_{xc} is defined as the one-body multiplicative potential with which the solution of Eq. (2) reproduces the density of the interacting system, and it is the only part that needs to be approximated in practice. One can obtain information about the excitations in the interacting system by propagating Eq. (2) under an external perturbative potential,[32] but the more convenient approach is to work in the frequency domain from the beginning.

The linear response function[33] $\chi = \delta n/\delta v_{\text{ext}}$ describes the first-order density change caused by a change in the external potential, and thus determines the optical spectrum. In TDDFT,[34] the response function in reciprocal space is obtained, in principle exactly, as

$$\chi_{\mathbf{GG}'}(\mathbf{q}, \omega) = \sum_{\mathbf{G}''}\left[\delta_{\mathbf{G}_1\mathbf{G}_2} - \sum_{\mathbf{G}_3}\chi_{s,\mathbf{G}_1\mathbf{G}_3}(\mathbf{q}, \omega)\right.$$
$$\left. \times f_{\text{Hxc},\mathbf{G}_3\mathbf{G}_2}(\mathbf{q}, \omega)\right]^{-1}_{\mathbf{GG}''}\chi_{s,\mathbf{G}''\mathbf{G}'}(\mathbf{q}, \omega), (3)$$

where χ_s is the linear response function of the Kohn-Sham system,[12] $f_{\text{Hxc}} = f_{\text{H}} + f_{\text{xc}}$ with the Hartree kernel $f_{\text{H}} = \delta v_{\text{H}}/\delta n$ (in reciprocal space, $f_{\text{H}} = 4\pi\delta_{\mathbf{GG}'}/|\mathbf{q}+\mathbf{G}|$), and the xc kernel $f_{\text{xc}} = \delta v_{\text{xc}}/\delta n$. All quantities in Eq. (3) are matrices in momentum space, where $\mathbf{q}$ belongs to the first Brillouin zone, and the $\mathbf{G}$'s are reciprocal lattice vectors.

The optical absorption spectrum of a periodic system is described by the macroscopic dielectric function ϵ_{M}.[6] One calculates ϵ_{M} from χ by

$$\epsilon_{\text{M}}(\omega) = \lim_{\mathbf{q}\to 0}\frac{1}{1 + 4\pi\chi_{00}(\mathbf{q}, \omega)/q^2}. \quad (4)$$

Calculating ϵ_{M} on a frequency grid yields the spectrum.

The so-called head ($\mathbf{G} = \mathbf{G}' = 0$) of the xc kernel gives the largest contribution to the change from χ_s to χ, and the contributions from bigger $\mathbf{G}$'s decay rapidly. Thus the sums in Eq. (3) can be restricted to a small number of reciprocal lattice vectors, which reduces the computational effort significantly.

One can select the frequency ω in Eq. (3), so the calculation can be focused on the region of interest instead of the entire spectrum. It might appear that in Eq. (3) one can choose any frequency resolution, but it is implicitly limited by the number of Kohn-Sham excitations included in χ_s. A part of the spectrum is directly obtained from this approach, but there is no way of knowing which Kohn-Sham excitations contribute to a specific peak. Considering the continuum nature of the spectra of periodic systems, these details are of course rarely needed. For excitons, however, the binding energies are not explicitly given in this approach, unlike in the much simpler Wannier model. Due to the discrete nature of bound excitons, the Kohn-Sham excitation composition is useful for interpretations; but this information is not available in this approach.

In finite systems the low-lying excitations are discrete, and there is a more efficient way to obtain them than

scanning the frequency range with Eq. (3). The idea is to describe electronic excitations as eigenmodes of the system.[35] The Casida equation[27] then transforms the TDDFT linear-response equation into the transition space spanned by single-particle Kohn-Sham excitations:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} -\mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}, \quad (5)$$

where the matrix elements of $\mathbf{A}$ and $\mathbf{B}$ are

$$A^{(ij)(mn)}(\omega) = (\epsilon_j - \epsilon_i)\delta_{im}\delta_{jn} + F_{\text{HXC}}^{(ij)(mn)}(\omega),$$
$$B^{(ji)(mn)}(\omega) = F_{\text{HXC}}^{(ji)(mn)}(\omega), \quad (6)$$

with the Hartree-exchange-correlation (Hxc) matrix F_{HXC} for spin-unpolarized systems

$$F_{\text{HXC}}^{(ij)(mn)}(\omega) = 2 \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \; \phi_i(\mathbf{r})\phi_j^*(\mathbf{r}) f_{\text{HXC}}(\mathbf{r}, \mathbf{r}', \omega)$$
$$\times \phi_m^*(\mathbf{r}')\phi_n(\mathbf{r}'). \quad (7)$$

The factor of 2 in F_{HXC} accounts for the spin and the ϕ's are the ground-state Kohn-Sham orbitals. The indices i, j, m, n all represent full sets of quantum numbers, where i, m denote occupied orbitals and j, n denote unoccupied orbitals.

Most of the currently available xc kernels are frequency independent, in which case Eq. (5) becomes an eigenvalue problem. The explicit matrix formulation of Eq. (5) is suitable for discrete excitations in finite systems. The excitation frequencies of the system are explicitly given by the eigenvalues ω. The eigenvector X together with Y describes how the Kohn-Sham excitations combine to form the excitation in the real system. The optical spectrum can be calculated with X and Y.[6] The widely used Tamm-Dancoff approximation (TDA) sets the matrix $\mathbf{B}$ to zero and hence neglects the correlation between excitations and de-excitations. We have shown that the TDA can often be a better choice for excitons than the exact calculation with Eq. (5),[26] and we therefore employ the TDA throughout this paper.

The difficulty of obtaining excitons in TDDFT mainly comes from the requirement on the xc kernel for periodic systems, that it needs a q^{-2} behavior in the $\mathbf{q} \to 0$ limit.[20] This long-range behavior is necessary in order to produce non-zero head ($\mathbf{G} = \mathbf{G}' = 0$) and wing ($\mathbf{G} = 0$ or $\mathbf{G}' = 0$) contribution to χ in Eq. (3) and to F_{XC} in Eq. (7). In periodic systems these contributions dominate over the so-called local-field effects [contributions from the body ($\mathbf{G} \neq 0$ and $\mathbf{G}' \neq 0$) of f_{xc}]. Common local and semi-local xc kernels, such as the adiabatic local-density approximation (ALDA), lack this long-range behavior. Several recently proposed functionals (such as the empirical long-range correction[21], the non-empirical bootstrap kernel[28] and the non-empirical meta-GGA kernel[19]) have the correct long-range behavior; hence, they are promising choices for the accurate calculation of excitons in TDDFT. Due to its discrete nature, the Casida equation approach is rarely used for periodic systems. For calculating exciton binding energies, however, it is preferable over the usual response-function approach.

III. METHOD

In this section we present the details of how we apply our TDDFT approach for calculating exciton binding energies. Within the TDA and using the adiabatic approximation for the xc kernel, Eq. (5) becomes

$$\sum_{(mn)} \left[\delta_{im}\delta_{jn}(\epsilon_j - \epsilon_i) + F_{\text{HXC}}^{(ij)(mn)} \right] \rho^{(mn)}(\omega) = \omega\rho^{(ij)}(\omega). \quad (8)$$

We only consider optical excitations which have no momentum transfer. Thus only the $\mathbf{q} = 0$ part of the xc kernel is involved. The xc matrix element in reciprocal space for spin-unpolarized systems is given by

$$F_{\text{XC}}^{(ij\mathbf{k})(mn\mathbf{k}')} = \frac{2}{V} \sum_{\mathbf{G}\mathbf{G}'} f_{\text{xc},\mathbf{G}\mathbf{G}'}(\mathbf{q} = 0)$$
$$\times \left\langle j\mathbf{k} \left| e^{i\mathbf{G}\cdot\mathbf{r}} \right| i\mathbf{k} \right\rangle \left\langle m\mathbf{k}' \left| e^{-i\mathbf{G}'\cdot\mathbf{r}} \right| n\mathbf{k}' \right\rangle, (9)$$

where V is the volume of the crystal, $\mathbf{k}$, $\mathbf{k}'$ are Bloch wavevectors of orbitals, and i, j, m, n are band indices. Since the matrix element $\left\langle j\mathbf{k} \left| e^{i\mathbf{G}\cdot\mathbf{r}} \right| i\mathbf{k} \right\rangle$ vanishes as $\mathbf{G} \to 0$, the contributions of the head ($\mathbf{G} = \mathbf{G}' = 0$) and of the wings ($\mathbf{G} = 0$ or $\mathbf{G}' = 0$) need to be evaluated analytically. f_{xc} must diverge as q^{-2} for the head and as q^{-1} for the wings for these to have a nonzero contribution. In this work, we use the ABINIT pseudopotential band structure code for the Kohn-Sham ground state.[36] Due to the presence of pseudopotentials, the above matrix element for $\mathbf{G} = 0$ must be replaced by[37]

$$\left\langle j\mathbf{k} \left| e^{i\mathbf{G}\cdot\mathbf{r}} \right| i\mathbf{k} \right\rangle \to \frac{\langle j\mathbf{k} | \hat{p} - i[\hat{r}, V_{\text{nl}}] | i\mathbf{k} \rangle}{\epsilon_{j\mathbf{k}} - \epsilon_{i\mathbf{k}}}, \quad (10)$$

where $\hat{p}$ is the momentum operator, $\hat{r}$ is the position operator, and V_{nl} is the nonlocal part of the pseudopotential.

A. XC kernels

We use the following adiabatic xc kernels in our study: the long-range correction,[21] the bootstrap kernel,[28] and the PGG kernel for singlet excitons,[38,39] and the hybrid kernel by Burke et al. for triplet excitons.[40]

The long-range correction kernel is defined as

$$f_{\text{XC}}^{\text{LRC}}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = -\frac{\alpha}{|\mathbf{q} + \mathbf{G}|^2}\delta_{\mathbf{G}\mathbf{G}'}, \quad (11)$$

where α is a material-dependent parameter. In Ref. 21, an empirical formula was proposed for determining α:

$$\alpha = 4.615\epsilon_\infty^{-1} - 0.213, \quad (12)$$

where ϵ_∞ is the high-frequency dielectric constant. The purpose of this empirical formula is to reproduce the continuum spectrum; here, we test its effect on the exciton binding energy, which would be too small to be resolved

in common response-function calculations.[21] For comparison, we will also fit α with respect to the experimental exciton binding energies.

The PGG kernel is a real-space kernel approximating the exact exchange kernel. In real space, it is defined as[38,39]

$$f_{\mathrm{xc}}^{\mathrm{PGG}}(\mathbf{r}, \mathbf{r}') = -\frac{2\left|\sum_{i\mathbf{k}}^{\mathrm{occ.}} \phi_{i\mathbf{k}}^*(\mathbf{r})\phi_{i\mathbf{k}}(\mathbf{r}')\right|^2}{|\mathbf{r}-\mathbf{r}'|\, n(\mathbf{r})n(\mathbf{r}')}, \qquad (13)$$

where n is the ground-state electronic density. We convert the PGG kernel into reciprocal space for its use in Eq. (9). The Kohn-Sham orbitals in Eq. (13) have the Bloch form,

$$\phi_{i\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_{\mathrm{cell}}}} u_{i\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}, \qquad (14)$$

where N_{cell} is the number of unit cells in the crystal, and $u_{i\mathbf{k}}(\mathbf{r})$ is the Bloch function. $f_{\mathrm{xc}}^{\mathrm{PGG}}$ can then be written as

$$f_{\mathrm{xc}}^{\mathrm{PGG}}(\mathbf{r}, \mathbf{r}') = -\sum_{i\mathbf{k}}^{\mathrm{occ.}}\sum_{m\mathbf{k}'}^{\mathrm{occ.}} \frac{2e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{r}-\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|} H_{i\mathbf{k}m\mathbf{k}'}(\mathbf{r}, \mathbf{r}'), \qquad (15)$$

where $H_{i\mathbf{k}m\mathbf{k}'}(\mathbf{r}, \mathbf{r}')$ is periodic within one unit cell and defined as

$$H_{i\mathbf{k}m\mathbf{k}'}(\mathbf{r}, \mathbf{r}') = \frac{u_{i\mathbf{k}}^*(\mathbf{r})u_{i\mathbf{k}}(\mathbf{r}')u_{m\mathbf{k}'}(\mathbf{r})u_{m\mathbf{k}'}^*(\mathbf{r}')}{N_{\mathrm{cell}}^2 n(\mathbf{r})n(\mathbf{r}')}. \qquad (16)$$

The Fourier transform of $f_{\mathrm{xc}}^{\mathrm{PGG}}$ yields

$$f_{\mathrm{xc}}^{\mathrm{PGG}}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = -\frac{1}{V}\sum_{i\mathbf{k}}^{\mathrm{occ.}}\sum_{m\mathbf{k}'}^{\mathrm{occ.}}\sum_{\mathbf{G}_0} \frac{8\pi}{|\mathbf{q}-(\mathbf{k}'-\mathbf{k})+\mathbf{G}_0|^2}$$
$$\times \tilde{H}_{i\mathbf{k}m\mathbf{k}'}(\mathbf{G}-\mathbf{G}_0, \mathbf{G}'-\mathbf{G}_0), \qquad (17)$$

where $\tilde{H}$ is obtained by numerical Fourier transform of expression (16) within one unit cell. For simplicity, we ignore the local-field effects and only use the head of the PGG kernel, which is given by

$$f_{\mathrm{xc}}^{\mathrm{PGG}}(\mathbf{q}, 0, 0) = -\frac{8\pi}{V}\sum_{i,m,\mathbf{k}}^{\mathrm{occ.}} \frac{\tilde{H}_{i\mathbf{k}m\mathbf{k}}(0,0)}{|\mathbf{q}|^2}. \qquad (18)$$

The PGG kernel is orbital dependent and involves a sum over all occupied orbitals. It is not obvious whether the pseudopotential formalism is directly compatible with this kernel since it does not properly include the core states; this will be the subject of future study. For the time being, we use all the occupied pseudo-bands for constructing the PGG kernel.

The so-called bootstrap kernel[28] is a recently proposed non-empirical adiabatic xc kernel, designed to be able to treat excitons:

$$f_{\mathrm{xc,sym}}^{\mathrm{bootstrap}}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = \frac{\epsilon_{\mathrm{sym}}^{-1}(\mathbf{q}, \mathbf{G}, \mathbf{G}')}{\chi_{s,\mathrm{sym}}(\mathbf{q}, \mathbf{G}=\mathbf{G}'=0)}, \qquad (19)$$

where $f_{\mathrm{xc,sym}}$, $\epsilon_{\mathrm{sym}}^{-1}$ and $\chi_{s,\mathrm{sym}}$ are the xc kernel, inverse dielectric function and Kohn-Sham linear response function in their symmetric forms, respectively, defined as

$$f_{\mathrm{xc,sym}}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = v_{\mathbf{G}}^{-1/2}(\mathbf{q})f_{\mathrm{xc}}(\mathbf{q}, \mathbf{G}, \mathbf{G}')v_{\mathbf{G}'}^{-1/2}(\mathbf{q}) \quad (20)$$

$$\epsilon_{\mathrm{sym}}^{-1}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = v_{\mathbf{G}}^{-1/2}(\mathbf{q})\epsilon^{-1}(\mathbf{q}, \mathbf{G}, \mathbf{G}')v_{\mathbf{G}'}^{1/2}(\mathbf{q}), \quad (21)$$

$$\chi_{\mathrm{sym}}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = v_{\mathbf{G}}^{1/2}(\mathbf{q})\chi(\mathbf{q}, \mathbf{G}, \mathbf{G}')v_{\mathbf{G}'}^{1/2}(\mathbf{q}), \quad (22)$$

where $v_{\mathbf{G}}(\mathbf{q}) = 4\pi/|\mathbf{q}+\mathbf{G}|^2$ is the Coulomb potential. $\epsilon_{\mathrm{sym}}^{-1}$ in Eq. (19) is calculated as

$$\epsilon_{\mathrm{sym}}^{-1} = 1 + \chi_{\mathrm{sym}}$$
$$= 1 + (1 - \chi_{s,\mathrm{sym}}f_{\mathrm{HXC,sym}})^{-1}\chi_{s,\mathrm{sym}}, \qquad (23)$$

where all quantities in Eq. (23) are matrices in $\mathbf{G}$ and $\mathbf{G}'$. Equations (23) and (19) are iteratively evaluated until self-consistency is achieved. Since the head and the wings of f_{xc} diverge as $\mathbf{q} \to 0$ (which is important for excitons), f_{xc} cannot be used directly in the iteration due to numerical difficulties. The symmetric forms ensure that no troubling singularities are involved.

So far, we have neglected the spin. In principle, a noncollinear spin formulation for the xc kernel[12,41] is needed to treat singlet and triplet excitations on the same ground. For spin-unpolarized systems, however, one can define singlet and triplet xc kernels as

$$f_{\mathrm{xc}}^{\mathrm{singlet}} = \frac{f_{\mathrm{xc}}^{\uparrow\uparrow} + f_{\mathrm{xc}}^{\uparrow\downarrow}}{2}, \quad f_{\mathrm{xc}}^{\mathrm{triplet}} = \frac{f_{\mathrm{xc}}^{\uparrow\uparrow} - f_{\mathrm{xc}}^{\uparrow\downarrow}}{2}, \qquad (24)$$

where $f_{\mathrm{xc}}^{\sigma\sigma'} = \delta v_{\mathrm{xc}\sigma}/\delta n_{\sigma'}$ is the spin-dependent xc kernel. Only $f_{\mathrm{xc}}^{\uparrow\uparrow}$ and $f_{\mathrm{xc}}^{\uparrow\downarrow}$ are involved because $f_{\mathrm{xc}}^{\downarrow\downarrow} = f_{\mathrm{xc}}^{\uparrow\uparrow}$ and $f_{\mathrm{xc}}^{\downarrow\uparrow} = f_{\mathrm{xc}}^{\uparrow\downarrow}$ in spin-unpolarized systems. One calculates singlet and triplet excitations by performing two separate TDDFT calculations with $f_{\mathrm{xc}}^{\mathrm{singlet}}$ and $f_{\mathrm{xc}}^{\mathrm{triplet}}$ (the triplet calculation does not include the Hartree kernel). In the spin-dependent case, the important property for excitons is the exchange splitting Δ_{x}, defined as

$$\Delta_{\mathrm{x}} = E_b^{\mathrm{triplet}} - E_b^{\mathrm{singlet}}. \qquad (25)$$

The bootstrap xc kernel was originally developed for the spin-independent case. Since it is not defined via a functional derivative, there is no unique way to make it spin dependent. We propose a plausible spin-dependent generalization of the bootstrap kernel in such a way that the singlet result does not change during the self-consistent procedure. The idea is to replace $\chi_{s,\mathrm{sym}}^{-1}(\mathbf{q}, \mathbf{G} = \mathbf{G}' = 0)$ in Eq. (19) by a matrix $M_{\sigma\sigma'}$:

$$f_{\mathrm{xc,sym},\sigma\sigma'}^{\mathrm{bootstrap}}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = \sum_{\sigma''\mathbf{G}''} \epsilon_{\mathrm{sym},\sigma\sigma''}^{-1}(\mathbf{q}, \mathbf{G}, \mathbf{G}'')$$
$$\times M_{\sigma''\sigma'}(\mathbf{q}, \mathbf{G}'', \mathbf{G}'), \qquad (26)$$

where the spin-dependent inverse dielectric function ϵ^{-1} for a spin-unpolarized system can be defined as

$$\epsilon_{\sigma\sigma'}^{-1} = \delta_{\sigma\sigma'} + \sum_{\sigma''} v_{\sigma\sigma''}\chi_{\sigma''\sigma'}. \qquad (27)$$

The Coulomb interaction is spin-independent ($v_{\sigma\sigma''} = v$), so $\epsilon_{\text{sym}}^{-1}$ in Eq. (27) becomes

$$\epsilon_{\text{sym},\sigma\sigma'}^{-1} = \delta_{\sigma\sigma'} + \chi_{\text{sym}}^{\uparrow\uparrow} + \chi_{\text{sym}}^{\uparrow\downarrow}. \tag{28}$$

To ensure that $f_{\text{xc}}^{\text{singlet}} = f_{\text{xc}}^{\text{bootstrap}}$ during and after self-consistency, it is straightforward to show that the matrix $M_{\sigma\sigma'}$ must satisfy the following conditions:

$$M_{\sigma\neq\sigma'}(\mathbf{q}, \mathbf{G} = \mathbf{G}') = -M_{\sigma=\sigma'}(\mathbf{q}, \mathbf{G} = \mathbf{G}')$$
$$+ 2\chi_{s,\text{sym}}^{-1}(\mathbf{q}, \mathbf{G} = \mathbf{G}' = 0), \tag{29}$$
$$M_{\sigma\neq\sigma'}(\mathbf{q}, \mathbf{G} \neq \mathbf{G}') = -M_{\sigma=\sigma'}(\mathbf{q}, \mathbf{G} \neq \mathbf{G}'). \tag{30}$$

This ensures that the singlet xc kernel reproduces the bootstrap kernel, but it also has consequences for the triplet xc kernel. If the $M_{\sigma\sigma'}$ matrix is the same for all steps of the iteration, it is easy to show that during the iteration $f_{\text{xc}}^{\text{triplet}}$ would not change, and it can be determined without any iterative procedure as

$$f_{\text{xc,sym}}^{\text{triplet}}(\mathbf{q}, \mathbf{G}, \mathbf{G}') = \frac{1}{2}\left[M_{\uparrow\uparrow}(\mathbf{q}, \mathbf{G}, \mathbf{G}') - M_{\uparrow\downarrow}(\mathbf{q}, \mathbf{G}, \mathbf{G}')\right]. \tag{31}$$

$f_{\text{xc}}^{\text{triplet}}$ is determined self-consistently only if $M_{\sigma\sigma'}$ depends on f_{xc} of the previous iteration step.

Burke, Petersilka, and Gross[40] proposed a hybrid spin-dependent xc kernel, where

$$f_{\text{xc},\uparrow\uparrow}^{\text{hybrid}} = f_{\text{xc},\uparrow\uparrow}^{\text{PGG}}, \tag{32}$$
$$f_{\text{xc},\uparrow\downarrow}^{\text{hybrid}} = f_{\text{xc},\uparrow\downarrow}^{\text{ALDA}}. \tag{33}$$

This hybrid kernel yields rather accurate singlet-triplet splittings as well as excitations frequencies in finite system. Inspired by this, we propose to calculate the singlet-triplet splitting of excitons with a similar hybrid kernel. Since the bootstrap kernel is a parameter-free xc kernel that has good performance for exciton binding energies in several tested systems, we use the bootstrap kernel as the singlet xc kernel:

$$f_{\text{xc},\uparrow\uparrow}^{\text{bootstrap}} = 2f_{\text{xc}}^{\text{bootstrap}} - f_{\text{xc},\uparrow\downarrow}^{\text{ALDA}}, \tag{34}$$
$$f_{\text{xc},\uparrow\downarrow}^{\text{bootstrap}} = f_{\text{xc},\uparrow\downarrow}^{\text{ALDA}}. \tag{35}$$

The singlet exciton binding energy retains the result of the bootstrap kernel. This modified hybrid kernel is effectively an instance of the generalized spin-dependent bootstrap kernel, where

$$M_{\uparrow\uparrow} = f_{\text{xc,sym}}^{\text{bootstrap}} - f_{\text{xc,sym},\uparrow\downarrow}^{\text{ALDA}} + 2\chi_{s,\text{sym}}^{-1}, \tag{36}$$

and $M_{\uparrow\downarrow}$ is determined by Eqs. (29) and (30).

B. Computational aspects and numerical details

Let us now briefly summarize the computational aspects of our exciton calculations; more technical details will be presented elsewhere.[42]

An LDA ground-state calculation is carried out with the ABINIT pseudopotential code.[36] The ground-state band structure and Bloch functions are taken as the input to our TDDFT calculations. Due to the absence of the derivative discontinuity, the LDA Kohn-Sham gap is too small to approximate the quasiparticle gap.[43] This introduces big errors in the corresponding TDDFT calculation, since adiabatic xc kernels cannot change the gap.[44] A frequency-dependent kernel together with a good ground-state xc functional would be required to fully treat the gap problem in TDDFT. However, since our focus is on the exciton binding energies and not on the gap itself, we shift the gap to its corresponding experimental value by applying a simple scissor operator[45] to the conduction bands, and we apply a corresponding correction to the momentum matrix elements.[46] For xc kernels that explicitly depend on the density, we use the pseudodensity with the correction described in Ref. 47.

The F_{xc} matrix in Eq. (9) is represented in the transition space of Kohn-Sham excitations. It has the dimension $N_v \times N_c \times N_{\mathbf{k}}$, where v stands for valence bands, c stands for conduction bands, and $N_{\mathbf{k}}$ is the number of $\mathbf{k}$-grid points in the Brillouin zone. To achieve convergence, the dimension must be large, so a Casida-equation-type calculation is computationally more demanding than the usual response-function calculation; in particular, storage of a large matrix is required. For this reason, Casida-equation-type calculations are not usually done for periodic systems. In contrast, a response-function calculation processes matrices in reciprocal space; the dimension of the matrix equals the number of reciprocal lattice vectors used in the calculation, which is much smaller than the size of the F_{xc} matrix [Eq. (9)] required for convergence.

According to the Wannier model, excitons are dominated by single-particle (Kohn-Sham) excitations near the band edge for direct-gap solids. Although strictly speaking the Wannier model refers to quasiparticle bands instead of Kohn-Sham bands, the Kohn-Sham band structure is similar to the quasiparticle band structure near the Fermi level (aside from having the wrong gap).[21] Thus for direct-gap solids, only the highest valence bands and the lowest conduction bands are needed in the calculation (including degeneracies at the Γ point).

With only a few bands used, the dimension of the matrices in Eq. (5) is vastly reduced, so the eigenvalue problem can be solved with acceptable cost. For the same reason, we also only include excitations between these bands in the Kohn-Sham response function used in the bootstrap kernel. Although this restriction to a few bands near the band gap is sufficient for describing excitons, this would yield unsatisfactory continuum spectra; but those are not our concern in this work, since they can be calculated much better with the standard response-function approach of TDDFT.

To make the numerical problem more manageable for resource-limited environments, the storage of the large matrices can be distributed among different nodes of a computer cluster, and we use the ScaLAPACK[48] package

to manipulate the distributed matrix. Since we only need the first exciton binding energy, we can further simplify the eigenvalue problem by using an iterative eigenvalue solver such as FEAST[49] to converge only the eigenvalue for the exciton instead of all the excitations. Iterative eigenvalue solvers require a predefined range of the desired eigenvalues, which would require knowledge about the result before it is obtained. But in our case the range of frequency is conveniently chosen from zero to the band gap, since excitonic excitations are always below the band gap. With all the techniques described in this section, Casida-equation-like calculations for periodic solids become practically feasible.

We check convergence against the following parameters: the number of bands in the calculation, the **k**-grid for the ground state, and the reciprocal lattice vectors in constructing the matrix in Eq. (8).

For all systems under consideration, the highest valence band has p-character and is triply degenerate at the Γ point, while there is no degeneracy at the Γ point for the lowest conduction band. Thus we only include 3 valence bands and 1 conduction band in Eq. (8) and in the Kohn-Sham response function χ_s for the bootstrap kernel. We tested the convergence with respect to number of bands, and we found that the effect in the exciton binding energy from increasing the number of valence bands is much smaller than that of increasing the number of **G**-vectors. We test convergence against the TDDFT response-function calculations in Ref. 28, which by nature include much more bands than we use here. The excitons are strong enough in Ar and LiF to be resolved with the response-function approach, and our calculation with three valence and one conduction bands produces exciton binding energies very close to those reported in Ref. 28 (see Table I). We thus conclude that our few-band approach is sufficient for exciton binding energies.

We find that for strongly bound Frenkel excitons in insulators, a small **k**-grid such as a $10 \times 10 \times 10$ Monkhorst-Pack grid[50] is sufficient for the convergence of the binding energy. In the case of weakly bound Wannier excitons in semiconductors, the convergence is much slower and requires at least a $18 \times 18 \times 18$ grid. This result is not surprising, since Frenkel excitons are local in real space, which means they are diffuse in reciprocal space, and therefore require less resolution to be well-described in the reciprocal space than Wannier excitons.

Several previous TDDFT studies (within the response-function approach) state that convergence is achieved for semiconductors with grids like $15 \times 15 \times 15$.[21,28] However, in these cases convergence is to be understood with respect to the continuum spectra instead of the exciton binding energies. We find that with a $15 \times 15 \times 15$ grid, the maximum relative error in exciton binding energies for semiconductors studied in this work is 139%. We therefore calculate zincblende materials with a $18 \times 18 \times 18$ grid, wurtzite materials with a $20 \times 20 \times 20$ grid, and insulators with a $10 \times 10 \times 10$ grid. The ground-state cal-

culation with a bigger **k**-grid is feasible since the number of effective **k**-points can be greatly reduced by symmetry, but this is not the case for TDDFT, where the **k**-points in the entire first Brillouin zone must be included.

Excitons are usually described as electron-hole pairs and are modeled with parabolic bands. This may suggest that one can get away with using only **k**-points near the Γ-point ($\mathbf{k} = 0$), which would greatly decrease the size of the problem. This approach was employed by Rohlfing and Louie in a BSE study.[51] In a TDDFT context, however, for GaAs including 62% of the **k**-points (centered at the Γ-point) induces a 74% relative error, and even including 95% of the **k**-points still induces a 5% error, and the benefit of calculation speed is diminishing. We confirm the result with BSE and TDDFT calculations for an 1D Kronig-Penney model,[26] where we find that only including k-points near $k = 0$ induces a relative error three times larger in TDDFT than in BSE. This can be understood by analyzing the coupling matrix of TDDFT [F_{xc} in Eq. (9)] and BSE (Ref. 26): the equivalent object of F_{xc} in BSE is dominated by its diagonal ($\mathbf{k} = \mathbf{k}'$) part, so only taking the **k**-points near the Γ-point still retains its shape. In TDDFT this is not the case. Excitons are known to have collective character, but this discrepancy between model systems and excitons in real materials points to a surprisingly high degree of collectiveness when represented with single-particle Kohn-Sham excitations, since Kohn-Sham excitations contribute over the entire Brillouin zone.

The head of the xc kernel makes the largest contribution in Eq. (8); the other contributions can be usually ignored without loss of accuracy. We find that this is also true for the exciton binding energy. We checked the error in the exciton binding energy introduced by only using the head of the xc kernel, and the error is about 1% in most cases, and less than 5% throughout. Thus we only use the head in most calculations, but in cases where the head vanishes (such as the ALDA part included in the hybrid kernel), we include **G**-vectors with length up to $2G_0$, with G_0 being the longest reciprocal cell vector. The construction of the bootstrap kernel involves matrix operations in the reciprocal space, so we also use **G**-vectors up to $2G_0$ for it. After the bootstrap kernel is calculated, we only use its head in Eq. (8). It should be noticed that although this still yields acceptable accuracies for the exciton binding energy, only using the head would not produce more than one exciton.[26] If one needs an excitonic Rydberg series, the wings and body contribution of the xc kernel are necessary.

For the bootstrap kernel there is an additional convergence issue related to the number of bands that need to be included in the Kohn-Sham response function χ_s. For large-gap insulators, we only need to use four bands in the calculation of χ_s; For zincblende semiconductors, we have to use a total of 60 bands to achieve convergence. For wurtzite semiconductors, we use 10 valence bands and 40 conduction bands in the calculation.

TABLE I. Lowest singlet exciton binding energies E_b^{singlet} and singlet-triplet splittings Δ_{x}, calculated with TDDFT using various different xc kernels, and compared to experimental values from the literature. A star ($*$) means that no bound exciton was obtained from the calculation, "n.c." means that no calculation was performed.

Material[a]	GaAs	β-GaN	α-GaN	CdS	CdSe	Ar	Ne	LiF
Exp. gap (eV)	1.52	3.3	3.452	2.42	1.74	14.25	21.51	14.20
Exp. E_b^{singlet}[b]	3.27meV	26.0meV	20.4meV	28.0meV	15.0meV	1.90eV	4.08eV	1.6eV
Exp. Δ_{x}[c]	9.61μeV	—	—	—	49.78μeV	0.16eV	0.14eV	—
LRC empirical α[d]	0.211	0.6578	0.6496	0.6448	0.4721	2.697	—	2.191
LRC empirical E_b^{singlet}	0.8580meV	0.5143meV	$*$	0.5131meV	1.405meV	0.3043meV	—	1.136meV
LRC fit α	0.595	2.409	3.6285	4.244	2.144	21.45	96.5	9.5
$f_{\text{xc}}^{\text{bootstrap}}$ E_b^{singlet}	0.3318meV	0.1992meV	$*$	0.4610meV	0.8947meV	2.156eV	6.225eV	1.547eV
Corresponding LRC α[e]	0.08836	0.3048	0.2147	0.5895	0.3183	22.6324	126.673	9.32326
PGG E_b^{singlet}[f]	$*$	n.c.	n.c.	n.c.	n.c.	$*$	n.c.	$*$
Corresponding LRC α[e]	5.820×10^{-5}	n.c.	n.c.	n.c.	n.c.	3.924×10^{-4}	n.c.	3.851×10^{-4}
hybrid[g] Δ_{x}	37.65μeV	40.51μeV	$*$	n.c.	n.c.	0.03297eV	0.01287eV	0.5041meV

[a] Unless otherwise mentioned, zincblende materials are calculated with $18 \times 18 \times 18$ Monkhorst-Pack **k**-point grid, wurtzite materials are calculated with $20 \times 20 \times 20$ grid, and solid Ar, solid Ne, and LiF are calculated with $10 \times 10 \times 10$ grid.

[b] Experimental data from Refs. 52–59.

[c] Experimental data from Refs. 57, 59–61. No experimental data available for GaN, CdS, and LiF.

[d] Calculated using Eq. (12). The ϵ_∞^{-1} data is not available for solid Ne.

[e] The head of the xc kernel has the same form as the LRC.

[f] Local field effects included.

[g] See Eqs. (34) and (35).

IV. RESULTS

We consider several common direct-gap zincblende (GaAs, β-GaN) and wurtzite (α-GaN, CdS, CdSe) semiconductors, as well as insulators (LiF, solid Ar, solid Ne). Results are presented in Table I. The first three rows give experimental data on the band gap,[54,62–66] the binding energy E_b^{singlet} of the lowest singlet exciton,[52–59] and the singlet-triplet exchange splitting Δ_{x}.[57,59–61] The remaining rows of Table I show the results of our calculations.

The exciton binding energies calculated with the LRC kernel are generally found to be significantly too small if the empirical α is used, see Eq. (12); for α-GaN, there is not even a bound exciton. We therefore determine the LRC α parameter for the exciton binding energies by fitting to experimental data for E_b^{singlet}, and we find that they are quite different from the empirical formula for α. Ref. 21 argued that α must be proportional to ϵ_∞^{-1}, but we cannot confirm such a linear fit for α with our results. The sensitivity of the exciton binding energy with respect to α varies a lot for different materials. Though the empirical formula for α [Eq. (12)] was originally not developed to give accurate exciton binding energies, we find that calculations with empirical α still yield bound excitons (except for α-GaN). This may explain, at least in part, why these parameters lead to quite accurate spectra in the vicinity of the gap.

We next consider two nonempirical kernels, bootstrap and PGG. We find that the self-consistent procedure of the bootstrap kernel is very stable: even if we start the iteration with a different f_{xc} (instead of starting with no f_{xc}), we always converge to the same bootstrap kernel. We confirm that the bootstrap kernel produces accurate exciton binding energies for Frenkel excitons in Ar and LiF, as reported in Ref. 28. For Ne the bootstrap kernel overbinds by about 50%, but it still yields the correct order of magnitude for E_b^{singlet}. For Wannier excitons in the studied semiconductors, however, the bootstrap kernel fails to differentiate between different materials and in all cases yields exciton binding energies that are too low. On the other hand, the excitonic enhancement of the continuum spectrum is reported to be well-described by this kernel. This is understandable since the corresponding LRC α parameters for semiconductors are close to those given by the empirical formula Eq. (12).

The performance of the PGG kernel, which works well in finite systems, is disappointing: it does not produce any bound excitons at all, despite having a nonzero head contribution. The PGG kernel is an exchange-only kernel, and is known to bind quite strongly in finite systems,[38,40] so it is surprising that it does not yield any bound exciton in the cases we tested. One possible reason is that the pseudopotential treatment is not compatible with the explicit orbital dependence in the PGG kernel, since the contribution from core orbitals cannot be systematically included. Also it should be noted that while periodic systems are dominated by the head of the xc kernel, there is no corresponding effect in finite systems. This is because in finite systems the electron dynamics can be viewed as coming entirely from local-field effects. Thus, the strongly attractive nature of the PGG kernel in finite systems would at most translate into a strong body of the xc matrix in periodic systems (which, how-

ever, is irrelevant for excitons), but does not necessarily guarantee a strong head. This is indeed confirmed by calculating the LRC α that corresponds to the PGG kernel, which turns out to be orders of magnitude too weak (see the second-to-last row of Table I).

As we discussed in Section III A, not many long-range spin-dependent xc kernels for treating triplet excitons are known. Our hybrid kernel [Eqs. (34) and (35)] can be viewed as a special case of the generalized bootstrap kernel in Eq. (26), which performed well for singlet excitons. We find that the exchange splitting is of the right order of magnitude for GaAs, although somewhat too large. A similar Δ_x is found for β-GaN, but there is no experimental data available for comparison. Since α-GaN does not have a bound exciton with the bootstrap kernel, it is not possible to obtain a well-defined Δ_x with the hybrid kernel. No calculation was performed for CdS and CdSe due to excessive memory requirements. Finally, for the strongly bound excitons in the large-gap insulators Ar, Ne, and LiF, Δ_x comes out significantly too small.

Considering the fact that the singlet-triplet exchange splitting is essentially treated on an ALDA level, it is perhaps not surprising that the results for Δ_x with the hybrid kernel are not terribly accurate. Clearly, more sophisticated spin-dependent xc kernels for singlet and triplet excitons need to be developed.

V. CONCLUSION

In this paper we have introduced an alternative TDDFT approach for calculating excitonic binding energies in solids. We present the first converged Casida-equation-type TDDFT calculations for several materials, showing that such calculations are feasible for real periodic bulk systems. The approach yields exciton binding energies directly, rather than the optical spectrum. Although using only a few bands in general does not yield accurate continuum spectra, it is sufficient for the convergence of exciton binding energies. Binding energies of Frenkel excitons converge quickly with respect to the **k**-grid, while Wannier excitons require larger **k**-grids than usually seen in the literature. Although excitons are conventionally described as bound electron-hole pairs, only taking **k**-points near the Γ-point does not give a good description for excitons in TDDFT, suggesting very strong collective character when represented with Kohn-Sham excitations.

We test our formalism with several xc kernels. The LRC empirical formula, whose empirical parameter has been designed for reproducing the continuum spectrum, usually produces bound excitons as well, though the binding energies are generally too small. This is of course hardly surprising, because it is difficult to imagine how a single parameter could be sufficient to fit all aspects of the optical response. If one is interested in bound excitons rather than the continuum spectrum, the strength of the LRC kernel has to be increased.

The bootstrap kernel is generally accurate for Frenkel excitons, while it produces Wannier excitons that are somewhat too weakly bound. On the other hand, the PGG kernel does not yield any bound excitons at all. Thus, at present we do not know of any simple, nonempirical xc kernel that produces accurate bound Wannier excitons in solids. xc kernels derived from many-body theory[6,15,17,18] may be expected to perform better than the kernels we have studied here, but they are significantly more complex.

We also extended our formalism to triplet excitons, and derived a formula to generalize the bootstrap kernel to spin-dependent systems, with the hybrid kernel as a special case. This hybrid kernel yields the correct order of magnitude for singlet-triplet exchange splitting in some cases, but is in general not very quantitatively accurate. Thus, we have given a proof of principle that TDDFT is capable of producing reasonable exchange splittings in solids; the search for more accurate spin-dependent xc kernels for triplet excitons remains an important task for future investigations.

In summary, we have shown that TDDFT shows considerable promise for treating excitonic effects, but more accurate multipurpose xc kernels for solids are needed, particularly for spin-dependent phenomena. Our approach for directly calculating exciton binding energies will be convenient for facilitating such future developments.

ACKNOWLEDGEMENT

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