The Bethe-Salpeter Equation Formalism: From Physics to Chemistry

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Abstract

The Bethe-Salpeter equation (BSE) formalism is steadily asserting itself as a new efficient and accurate tool in the ensemble of computational methods available to chemists in order to predict optical excitations in molecular systems. In particular, the combination of the so-called GW approximation, giving access to reliable ionization energies and electron affinities, and the BSE formalism, able to model UV/Vis spectra, has shown to provide accurate singlet excitation energies with a typical error of 0.1–0.3 eV. With a similar computational cost as time-dependent density-functional theory (TD-DFT), BSE is able to provide an accuracy on par with the most accurate global and range-separated hybrid functionals without the unsettling choice of the exchange-correlation functional, resolving further known issues (e.g., charge-transfer excitations). In this Perspective article, we provide a historical overview of BSE, with a particular focus on its condensed-matter roots. We also propose a critical review of its strengths and weaknesses in different chemical situations.

Graphical TOC Entry

Introduction. In its press release announcing the attribution of the 2013 Nobel prize in Chemistry to Karplus, Levitt, and Warshel, the Royal Swedish Academy of Sciences concluded by stating “Today the computer is just as important a tool for chemists as the test tube. Simulations are so realistic that they predict the outcome of traditional experiments.”1 Martin Karplus’ Nobel lecture moderated this statement, introducing his presentation by a 1929 quote from Dirac emphasizing that laws of quantum mechanics are “much too complicated to be soluble”, urging scientists to develop “approximate practical methods”. This is where the electronic structure community stands, attempting to develop robust approximations to study with increasing accuracy the properties of ever more complex systems. The study of optical excitations (also known as neutral excitations in condensed-matter systems), from molecules to extended solids, has witnessed the development of a large number of such approximate methods with numerous applications to...
a large variety of fields, from the prediction of the colour of precious metals for jewellery, to the understanding, e.g., of the basic principles behind organic photovoltaics, photocatalysis and DNA damage under irradiation. The present Perspective aims at describing the current status and upcoming challenges for the Bethe-Salpeter equation (BSE) formalism that, while sharing many features with time-dependent density-functional theory (TD-DFT), including computational scaling with system size, relies on a very different formalism, with specific difficulties but also potential solutions to known TD-DFT issues.

Theory. The BSE formalism belongs to the family of Green’s function many-body perturbation theories (MBPT) together with, for example, the algebraic-diagrammatic construction (ADC) techniques or the polarization propagator approaches (like SOPPA) in quantum chemistry. While the one-body density stands as the basic variable in density-functional theory (DFT), the pillar of Green’s function MBPT is the (time-ordered) one-body Green’s function

\[ G(x, x'; \omega) = \sum_x \frac{f_x(x)f_x^*(x')}{\omega - \epsilon_x + i\eta \times \text{sgn}(\epsilon_x - \mu)}. \] (3)

where \( \mu \) is the chemical potential, \( \eta \) is a positive infinitesimal, \( \epsilon_x = E^{N+1}_x - E^N_x \) for \( \epsilon_x > \mu \), and \( \epsilon_x = E^N_x - E^{N-1}_x \) for \( \epsilon_x < \mu \). Here, \( E^N_x \) is the total energy of the \( s \)th excited state of the \( N \)-electron system. The \( f_x \)’s are the so-called Lehmann amplitudes that reduce to one-body orbitals in the case of single-determinant many-body wave functions (see below). Unlike KS eigenvalues, the poles of the Green’s function \( \{\epsilon_x\} \) are proper addition/removal energies of the \( N \)-electron system, leading to well-defined ionization potentials and electronic affinities. In contrast to standard ASCF techniques, the knowledge of \( G \) provides the full ionization spectrum, as measured by direct and inverse photoemission spectroscopy, not only that associated with frontier orbitals.

Using the equation-of-motion formalism for the creation/destruction operators, it can be shown formally that \( G \) verifies

\[ \left[ \frac{\partial}{\partial r_1} - h(r_1) \right] G(1, 2) - \int d3 \Sigma(1,3)G(3,2) = \delta(1,2), \] (4)

where we introduce the composite index, e.g., \( 1 \equiv (x_1t_1) \). Here, \( \delta \) is Dirac’s delta function, \( h \) is the one-body Hartree Hamiltonian and \( \Sigma \) is the so-called exchange-correlation (xc) self-energy operator. Using the spectral representation of \( G \) [see Eq. (3)], dropping spin variables for simplicity, one gets the familiar eigenvalue equation, i.e.,

\[ h(r)f_x(r) + \int d r' \Sigma(r, r'; \epsilon_x)f_x(r') = \epsilon_x f_x(r), \] (5)

which formally resembles the KS equation with the difference that the self-energy \( \Sigma \) is non-local, energy-dependent and non-hermitian. The knowledge of \( \Sigma \) allows to access the true addition/removal energies, namely the entire spectrum of occupied and virtual electronic energy levels, at the cost of solving a generalized one-body eigenvalue equation.

The GW self-energy. While the equations reported above are formally exact, it remains to provide an expression for the xc self-energy operator \( \Sigma \). This is where Green’s function practical theories differ. Developed by Lars Hedin in 1965 with application to the interacting homogeneous electron gas, the GW approximation follows the path of linear response by considering the variation of \( G \) with respect to an external perturbation (see Fig. 1). The resulting equation, when compared with the equation for the time-evolution of \( G \) [see Eq. (4)], leads to a formal expression for the self-energy

\[ \Sigma(1,2) = i \int d34 G(1,4)W(3,1^+)\Gamma(42,3), \] (6)

where \( W \) is the dynamically-screened Coulomb potential and \( \Gamma \) is the so-called “vertex” function. The notation \( 1^+ \) means
that the time \( t_1 \) is taken at \( t_1^* = t_1 + 0^+ \) for sake of causality, where \( 0^+ \) is a positive infinitesimal. The neglect of the vertex, i.e., \( \Gamma(23, 4) = \delta(23)\delta(24) \), leads to the so-called GW approximation of the self-energy
\[
\Sigma^{GW}(1, 2) = iG(1, 2)W(2, 1^+),
\]
that can be regarded as the lowest-order perturbation in terms of the screened Coulomb potential \( W \) with
\[
W(1, 2) = \chi(1, 2) + \int d^3v \chi(1, 3)\chi_0(3, 4)W(4, 2),
\]
\[
\chi_0(1, 2) = -iG(1, 2^+)G(2, 1^+),
\]
where \( \chi_0 \) is the independent electron susceptibility and \( \chi \) the bare Coulomb potential. Equation (8a) can be recast as
\[
W(1, 2) = \chi(1, 2) + \int d^3v \chi(1, 3)\chi(3, 4)v(4, 2),
\]
where \( \chi \) is the interacting susceptibility. In this latter expression, \( (\chi \chi)v \) represents the field created in (2) by the charge rearrangement of the N-electron system generated by a (unit) charge added in (1). As such, this term contains the effect of dielectric screening (or polarization in a quantum chemist language). As in a standard \( \Delta SCF \) calculation, the GW formalism contains the response of the N-electron system to an electron added (removed) to any virtual (occupied) molecular orbital, but without the restriction that only frontier orbitals can be tackled. This explains that the GW one-electron energies are proper addition/removal energies.

In practice, the input \( G \) and \( \chi_0 \) required to initially build \( \Sigma^{GW} \) are chosen as the “best” Green’s function and susceptibility that can be easily computed, namely the KS or Hartree-Fock (HF) ones where the \( \{e_p, f_p\} \) of Eq. (3) are taken to be KS (or HF) eigenstates. Taking then \( (\Sigma^{GW} - \Sigma^{KS}) \) as a correction to the KS xc potential \( V^{\text{xc}} \), a first-order correction to the input KS energies \( \{\epsilon^{KS}_p\} \) is obtained by solving the so-called quasiparticle equation
\[
\omega = \epsilon^p_{KS} + \langle \phi_p^{KS} | \Sigma^{GW}(\omega) - V^{\text{xc}} | \phi_p^{KS} \rangle.
\]
As a non-linear equation, the self-consistent quasiparticle equation (10) has various solutions associated with different spectral weights. The existence of a well defined quasiparticle energy requires a solution with a large spectral weight, i.e., close to unity, a condition not always fulfilled for states far away from the fundamental gap.22

Such an approach, where input KS energies are corrected to yield better electronic energy levels, is labeled as the single-shot, or perturbative, \( G_0W_0 \) technique. This simple scheme was used in the early GW studies of extended semiconductors and insulators,23-26 and surfaces,27-29 allowing to dramatically reduce the errors associated with KS eigenvalues in conjunction with common local or gradient-corrected approximations to the xc potential. In particular, the well-known “band gap” problem,30,31 namely the underestimation of the occupied to unoccupied bands energy gap at the local-density approximation (LDA) KS level, was dramatically reduced, bringing the agreement with experiment to within a few tenths of an eV with a computational cost scaling quartically with the system size (see below). A compilation of data for \( G_0W_0 \) applied to extended inorganic semiconductors can be found in Ref. 32.

Although \( G_0W_0 \) provides accurate results (at least for weakly/moderately correlated systems), it is strongly starting-point dependent due to its perturbative nature. For example, the quasiparticle energies, and in particular the HOMOLUMO gap, depends on the input KS eigenvalues. Tuning the starting point functional or applying a self-consistent GW scheme are two different approaches commonly employed to tackle this problem. We will comment further on this particular point below when addressing the quality of the BSE optical excitations.

Another important feature compared to other perturbative techniques, the GW formalism can tackle finite and periodic systems, and does not present any divergence in the limit of zero gap (metallic) systems.33 However, remaining a low-order perturbative approach starting with a single-determinant mean-field solution, it is not intended to explore strongly correlated systems.34

Neutral excitations. Like TD-DFT, BSE deals with the calculations of optical (or neutral) excitations, as measured by optical (e.g., absorption) spectroscopy. However, while TD-DFT starts with the variation of the charge density \( \rho(1) \) with respect to an external local perturbation \( U(1) \), the BSE formalism considers a generalized four-point susceptibility, or two-particle correlation function, that monitors the varia-
tion of the one-body Green’s function \( G(1,1') \) with respect to a non-local external perturbation \( U(2,2') \): \(^7\)

\[
\chi(1,2) \xrightarrow{\text{DFT}} \frac{\partial \rho(1)}{\partial U(2)} \rightarrow L(1,2;1',2') = \frac{\partial G(1,1')}{\partial U(2,2')},
\]

The formal relation \( \chi(1,2) = -iL(1,2;1',2') \) with \( \rho(1) = -iG(1,1') \) offers a direct bridge between the TD-DFT and BSE worlds. The equation of motion for \( G \) [see Eq. (4)] can be reformulated in the form of a Dyson equation

\[
G = G_0 + G_0(v_H + U + \Sigma)G,
\]

where it is customary to neglect the derivative \((\partial W/\partial G)\) that introduces again higher orders in \( W \). At that stage, the BSE kernel is fully dynamical, i.e., it explicitly depends on the frequency \( \omega \). Taking the static limit, i.e., \( W(\omega = 0) \), for the screened Coulomb potential, that replaces the static DFT xc kernel, and expressing Eq. (13) in the standard product space \{\( \phi_i(r) \phi_a(r') \)\} [where \( (i,j) \) are occupied spatial orbitals and \((a,b)\) are unoccupied spatial orbitals], leads to an eigenvalue problem similar to the so-called Casida equations in TD-DFT: \(^8\)

\[
\left( \begin{array}{cc} R & C \\ -C^* & -R^* \end{array} \right) \begin{pmatrix} X_m \ Y_m \end{pmatrix} = \Omega_m \begin{pmatrix} X_m \ Y_m \end{pmatrix},
\]

with electron-hole (eh) eigenstates written as

\[
\psi_m^{eh}(r_e, r_h) = \sum_{ia} \left[X_{ia} \phi_i(r_h) \phi_a(r_e) + Y_{ia} \phi_i(r_e) \phi_a(r_h)\right],
\]

where \( m \) indexes the electronic excitations. The \{\( \phi_{i/a} \)\} are typically the input (KS) eigenstates used to build the GW self-energy. They are here taken to be real in the case of finite-size systems. In the case of a closed-shell singlet ground state, the resonant and coupling parts of the BSE Hamiltonian read

\[
R_{a_i,b_j} = \left( \varepsilon_{a}^{GW} - \varepsilon_{i}^{GW} \right) \delta_{ij} \delta_{ab} + \kappa(ia|jb) - W_{ij,ab},
\]

\[
C_{ai,bj} = \kappa(ia|bj) - W_{ib,aj},
\]

with \( \kappa = 2 \) or 0 if one targets singlet or triplet excited states (respectively), and

\[
W_{ij,ab} = \int d\mathbf{r} d\mathbf{r}' \phi_i(r) \phi_j(r) W(r, r'+\omega = 0) \phi_a(r') \phi_b(r'),
\]

where we notice that the two occupied (virtual) eigenstates are taken at the same position of space, in contrast with the \((ia|jb)\) bare Coulomb term defined as

\[
(ia|jb) = \int d\mathbf{r} d\mathbf{r}' \phi_i(r) \phi_a(r) \nu(r-r') \phi_j(r') \phi_b(r').
\]

Neglecting the coupling term \( C \) between the resonant term \( R \) and anti-resonant term \(-R^*\) in Eq. (18), leads to the well-known Tamm-Dancoff approximation (TDA).

As compared to TD-DFT, i) the GW quasiparticle energies \{\( \varepsilon_{i/a}^{GW} \)\} replace the KS eigenvalues, and ii) the non-local
screened Coulomb matrix elements replaces the DFT xc kernel. We emphasize that these equations can be solved at exactly the same cost as the standard TD-DFT equations once the quasiparticle energies and screened Coulomb potential $W$ are inherited from preceding GW calculations. This defines the standard (static) BSE@GW scheme that we discuss in this Perspective, highlighting its pros and cons.

**Historical overview.** Originally developed in the framework of nuclear physics, the BSE formalism has emerged in condensed-matter physics around the 1960’s at the tight-binding level with the study of the optical properties of simple semiconductors. Three decades later, the first ab initio implementations, starting with small clusters, extended semiconductors, and wide-gap insulators, paved the way to the popularization in the solid-state physics community of the BSE formalism.

Following pioneering applications to periodic polymers and molecules, BSE gained much momentum in quantum chemistry with, in particular, several benchmarks on large molecular sets performed with the very same parameters (geometries, basis sets, etc) than the available higher-level reference calculations. Such comparisons were grounded in the development of codes replacing the plane-wave paradigm of solid-state physics by Gaussian basis sets, together with adequate auxiliary bases when resolution-of-the-identity (RI) techniques were used.

An important conclusion drawn from these calculations was that the quality of the BSE excitation energies is strongly correlated to the deviation of the preceding GW HOMO-LUMO gap

$$E_g^{GW} = E_{\text{LUMO}}^{GW} - E_{\text{HOMO}}^{GW},$$

with the experimental (photoemission) fundamental gap defined in Eq. (2).

Standard $G_0W_0$ calculations starting with KS eigenstates generated with (semi)local functionals yield much larger HOMO-LUMO gaps than the input KS gap

$$E_g^{KS} = E_{\text{LUMO}}^{KS} - E_{\text{HOMO}}^{KS},$$

but still too small as compared to the experimental value, i.e.,

$$E_g^{KS} \ll E_g^{G_0W_0} < E_g^{\text{fund}}.$$

Such a residual discrepancy has been attributed by several authors to “overscreening”, namely the effect associated with building the susceptibility $\chi$ based on a grossly underestimated (KS) band gap. This leads to a spurious enhancement of the screening or polarization and, consequently, to an underestimated $G_0W_0$ gap as compared to the (exact) fundamental gap. More prosaically, the $G_0W_0$ approach is constructed as a first-order perturbation theory, so by correcting a very “bad” zeroth-order KS system one cannot expect to obtain an accurate corrected gap. Such an underestimation of the fundamental gap leads to a similar underestimation of the optical gap $E_g^{opt}$, i.e., the lowest optical excitation energy:

$$E_g^{opt} = E_1^N - E_0^N = E_g^{\text{fund}} + E_B,$$

where $E_B$ accounts for the excitonic effect, that is, the stabilization induced by the attraction of the excited electron and its hole left behind (see Fig. 2).

Such a residual gap problem can be significantly improved by adopting xc functionals with a tuned amount of exact exchange that yield a much improved KS gap as a starting point for the GW correction. Alternatively, self-consistent approaches such as eigenvalue self-consistent (evGW) or quasiparticle self-consistent (qsGW) schemes, where corrected eigenvalues, and possibly orbitals, are reprojected onto the system, have been shown to lead to a significant improvement of the quasiparticle energies in the case of molecular systems, with the advantage of significantly removing the dependence on the starting point functional. As a result, BSE singlet excitation energies starting from such improved quasiparticle energies were found to be in much better agreement with reference calculations. For sake of illustration, an average error of 0.2 eV was found for the well-known Thiel et al. gathering 200 representative single excitations from a large variety of representative molecules. This is equivalent to the best TD-DFT results obtained by scanning a large variety of hybrid functionals with various amounts of exact exchange.

**Charge-transfer excited states.** A very remarkable success of the BSE formalism lies in the description of charge-transfer (CT) excitations, a notoriously difficult problem for TD-DFT adopting standard (semi-)local functionals. Similar difficulties emerge in solid-state physics for semiconductors where extended Wannier excitons, characterized by weakly overlapping electrons and holes (Fig. 3), cause a dramatic deficit of spectral weight at low energy. These difficulties can be ascribed to the lack of long-range electron-hole interaction with local xc functionals. It can be cured through an exact exchange contribution, a solution that explains the success of (optimally-tuned) range-separated hybrids for the description of CT excitations. The analysis of the screened Coulomb potential matrix elements in the BSE kernel reveals that such long-range (non-local) electron-hole interactions are properly described, including in environments where the screening reduces the long-range electron-hole interactions. The success of the BSE formalism to treat CT excitations has been demonstrated in several studies, opening the way to the modeling of key applications such as doping, photovoltaics or photocatalysis in organic systems.

**Combining BSE with PCM and QM/MM models.** The ability to account for the effect on the excitation energies of an electrostatic and dielectric environment (an electrode, a solvent, a molecular interface...) is an important step towards the description of realistic systems. Pioneering BSE studies demonstrated, for example, the large renormalization of charged and neutral excitations in molecular systems and nanotubes close to a metallic electrode or in bundles. Recent attempts to merge the GW and BSE formalisms with model polarizable environments at the PCM or QM/MM lev-
quasiparticle energies and BSE neutral excitations can be renormalized by the effect of the environment.

As emphasized above, the BSE eigenvalue equation in the single-excitation space [see Eq. (18)] is formally equivalent to that of TD-DFT or TD-HF. Searching iteratively for the lowest eigenstates yields the same $O(N^4_{orb})$ matrix-vector multiplication cost within BSE and TD-DFT. Concerning the construction of the BSE Hamiltonian, it is no more expensive than building its TD-DFT analogue with hybrid functionals, reducing again to $O(N^4_{orb})$ operations with standard RI techniques. Explicit calculation of the full BSE Hamiltonian in transition space can be avoided using density matrix perturbation theory, but not reducing the $O(N^4_{orb})$ scaling, but sacrificing further the knowledge of the eigenvectors. Exploiting further the locality of the atomic orbital basis, the BSE absorption spectrum can be obtained with $O(N^3_{orb})$ operations using iterative techniques. With the same restriction on the eigenvectors, a time-propagation approach, similar to that implemented for TD-DFT, combined with stochastic techniques to reduce the cost of building the BSE Hamiltonian matrix elements, allows quadratic scaling with respect to the systems size.

In practice, the main bottleneck for standard BSE calculations as compared to TD-DFT resides in the preceding $GW$ calculation that scales as $O(N^4_{orb})$ with system size using plane-wave basis sets or RI techniques, but with a rather large prefactor. The field of low-scaling $GW$ calculations is however witnessing significant advances. While the sparsity of, for example, the overlap matrix in the atomic orbital basis allows to reduce the scaling in the large size limit, efficient real-space grids and time techniques are blooming. Borrowing in particular the well-known Laplace transform approach used in quantum chemistry, together with a stochastic sampling of virtual states, this family of

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techniques allow to set up linear scaling $GW$ calculations.\textsuperscript{102} The separability of occupied and virtual states summations lying at the heart of these approaches are now spreading fast in quantum chemistry within the interpolative separable density fitting (ISDF) approach applied for calculating with cubic scaling the susceptibility needed in random-phase approximation (RPA) and $GW$ calculations.\textsuperscript{103–105} These ongoing developments pave the way to applying the $GW@BSE$ formalism to systems containing several hundred atoms on standard laboratory clusters.

The triplet instability challenge. The analysis of the singlet-triplet splitting is central to numerous applications such as singlet fission or thermally activated delayed fluorescence (TADF). From a more theoretical point of view, triplet instabilities that often plague the applicability of TD-DFT are intimately linked to the stability analysis of restricted closed-shell solutions at the HF\textsuperscript{106} and KS\textsuperscript{107} levels. While TD-DFT with range-separated hybrids can benefit from tuning the range-separation parameter(s) as a mean to act on the triplet instability,\textsuperscript{108} BSE calculations do not offer this pragmatic way-out since the screened Coulomb potential that builds the kernel does not offer any parameter to tune.

Benchmark calculations\textsuperscript{109,110} clearly concluded that triplets are notably too low in energy within BSE and that the use of the TDA was able to partly reduce this error. However, as it stands, the BSE accuracy for triplets remains rather unsatisfactory for reliable applications. An alternative cure was offered by hybridizing TD-DFT and BSE, that is, by adding to the BSE kernel the correlation part of the underlying DFT functional used to build the susceptibility and resulting screened Coulomb potential $W$.\textsuperscript{111}

The challenge of the ground-state energy. In contrast to TD-DFT which relies on KS-DFT as its ground-state analog, the ground-state BSE energy is not a well-defined quantity, and no clear consensus has been found regarding its formal definition. Consequently, the BSE ground-state formalism remains in its infancy with very few available studies for atomic and molecular systems.\textsuperscript{88,112–115}

A promising route, which closely follows RPA-type formalisms,\textsuperscript{116} is to calculate the ground-state BSE energy within the adiabatic-connection fluctuation-dissipation theorem (ACFDT) framework.\textsuperscript{117} Thanks to comparisons with both similar and state-of-art computational approaches, it was recently shown that the ACFDT@BSE@GW approach yields extremely accurate PES around equilibrium, and can even compete with high-order coupled cluster methods in terms of absolute ground-state energies and equilibrium distances.\textsuperscript{115} However, their accuracy near the dissociation limit remains an open question.\textsuperscript{112,113,118–120} Indeed, in the largest available benchmark study,\textsuperscript{113} encompassing the total energies of the atoms H–Ne, the atomization energies of the 26 small molecules forming the HEAT test set, and the bond lengths and harmonic vibrational frequencies of 3$d$ transition-metal monoxides, the BSE correlation energy, as evaluated within the ACFDT framework,\textsuperscript{117} was mostly discarded from the set of tested techniques due to instabilities (negative frequency modes in the BSE polarization propagator) and replaced by an approximate (RPAsX) approach where the screened-Coulomb potential matrix elements was removed from the resonant electron-hole contribution.\textsuperscript{113,121} Moreover, it was also observed in Ref. 115 that, in some cases, unphysical irregularities on the ground-state PES appear due to the appearance of discontinuities as a function of the bond length for some of the $GW$ quasiparticle energies. Such an unphysical behavior stems from defining the quasiparticle energy as the solution of the quasiparticle equation with the largest spectral weight in cases where several solutions can be found [see Eq. (10)]. We refer the interested reader to Refs. 22,122–125 for detailed discussions.

The challenge of analytical nuclear gradients. The features of ground- and excited-state potential energy surfaces (PES) are critical for the faithful description and a deeper understanding of photochemical and photophysical processes.\textsuperscript{126} For example, chemoluminescence and fluorescence are associated with geometric relaxation of excited states, and structural changes upon electronic excitation.\textsuperscript{127} Reliable predictions of these mechanisms, which have attracted much experimental and theoretical interest lately, require exploring the ground- and excited-state PES. From a theoretical point of view, the accurate prediction of excited electronic states remains a challenge,\textsuperscript{128} especially for large systems where state-of-the-art computational techniques (such as multiconfigurational methods)\textsuperscript{129} cannot be afforded. For the last two decades, TD-DFT has been the go-to method to compute absorption and emission spectra in large molecular systems.

In TD-DFT, the PES for the excited states can be easily and efficiently obtained as a function of the molecular geometry by simply adding the ground-state DFT energy to the excitation energy of the selected state. One of the strongest assets of TD-DFT is the availability of first- and second-order analytic nuclear gradients (i.e., the first- and second-order derivatives of the excited-state energy with respect to atomic displacements), which enables the exploration of excited-state PES.\textsuperscript{130}

A significant limitation of the BSE formalism, as compared to TD-DFT, lies in the lack of analytical nuclear gradients for both the ground and excited states, preventing efficient studies of many key excited-state processes. While calculations of the $GW$ quasiparticle energy ionic gradients is becoming increasingly popular,\textsuperscript{131–135} only one pioneering study of the excited-state BSE gradients has been published so far.\textsuperscript{136} In this seminal work devoted to small molecules (CO and NH$_3$), only the BSE excitation energy gradients were calculated, with the approximation that the gradient of the screened Coulomb potential can be neglected, computing further the KS-LDA forces as its ground-state contribution.
Beyond the static approximation. Going beyond the static approximation is a difficult challenge which has been, nonetheless, embraced by several groups. As mentioned earlier in this Perspective, most of BSE calculations are performed within the so-called static approximation, which substitutes the dynamically-screened (i.e., frequency-dependent) Coulomb potential $W(\omega)$ by its static limit $W(\omega = 0)$ [see Eq. (22)]. It is important to mention that diagonalizing the BSE Hamiltonian in the static approximation corresponds to solving a linear eigenvalue problem in the space of single excitations, while it is, in its dynamical form, a non-linear eigenvalue problem (in the same space) which is much harder to solve from a numerical point of view. In complete analogy with the ubiquitous adiabatic approximation in TD-DFT, one key consequence of the static approximation is that double (and higher) excitations are completely absent from the BSE optical spectrum, which obviously hampers the applicability of BSE as double excitations may play, indirectly, a key role in photochemistry mechanisms. Higher excitations would be explicitly present in the BSE Hamiltonian by “unfolding” the dynamical BSE kernel, and one would recover a linear eigenvalue problem with, nonetheless, a much larger dimension. Corrections to take into account the dynamical nature of the screening may or may not recover these multiple excitations. However, dynamical corrections permit, in any case, to recover, for transitions with a dominant single-excitation character, additional relaxation effects coming from higher excitations.

From a more practical point of view, dynamical effects have been found to affect the positions and widths of core-exciton resonances in semiconductors, rare gas solids, and transition metals. Thanks to first-order perturbation theory, Rohlfing and coworkers have developed an efficient way of taking into account the dynamical effects via a plasmon-pole approximation combined with TDA. With such a scheme, they have been able to compute the excited states of biological chromophores, showing that taking into account the electron-hole dynamical screening is important for an accurate description of the lowest $n \rightarrow \pi^*$ excitations. Studying PYP, retinal and GFP chromophore models, Ma et al. found that “the influence of dynamical screening on the excitation energies is about 0.1 eV for the lowest $\pi \rightarrow \pi^*$ transitions, but for the lowest $n \rightarrow \pi^*$ transitions the influence is larger, up to 0.25 eV.” Zhang et al. have studied the frequency-dependent second-order BSE kernel and they have observed an appreciable improvement over configuration interaction with singles (CIS), time-dependent Hartree-Fock (TDHF), and adiabatic TD-DFT results. Rebolini and Toulouse have performed a similar investigation in a range-separated context, and they have reported a modest improvement over its static counterpart. In these two latter studies, they also followed a (non-self-consistent) perturbative approach within TDA with a renormalization of the first-order perturbative correction.

Conclusion. Although far from being exhaustive, we hope that this Perspective provides a concise and fair assessment of the strengths and weaknesses of the BSE formalism of many-body perturbation theory. To do so, we have briefly reviewed the theoretical aspects behind BSE, and its intimate link with the underlying $GW$ calculation that one must perform to compute quasiparticle energies and the dynamically-screened Coulomb potential; two of the key input ingredients associated with the BSE formalism. We have then provided a succinct historical overview with a particular focus on its condensed-matter roots, and the lessons that the community has learnt from several systematic benchmark studies on large molecular systems. Several success stories are then discussed (charge-transfer excited states and combination with reaction field methods), before debating some of the challenges faced by the BSE formalism (computational cost, triplet instabilities, ambiguity in the definition of the ground-state energy, lack of analytical nuclear gradients, and limitations due to the static approximation). We hope that, by providing a snapshot of the ability of BSE in 2020, the present Perspective article will motivate a larger community to participate to the development of this alternative to TD-DFT which, we believe, may become a very valuable computational tool for the physical chemistry community.

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