Quantitative understanding the excited states of many-body systems, both extended and molecular, is a necessary step towards the design of materials with tailored (opto)electronic properties. Experimentally, photo-emission spectra (PES) directly probe the excitation energies of individual charge carriers and collective degrees of freedom. Describing these theoretically is a hard task, since it involves capturing both the simple quasiparticle (QP) behavior, as well as deviations thereof. In the former case, we identify a single QP regime (SQP) with a single sharp line per orbital/band. However, the simultaneous presence of several competing excitations corresponds to a multiple QP (MQP) regime. Understanding the latter is particularly important for quantum materials, since these exhibit intrinsically MQP phenomena 1–7.

In the MQP regime, identifying the physical origin of a given peak is still an open problem; even in “simple” systems, distinct theoretical treatments provide contradictory results. For example, there is an ongoing debate about the signatures of plasmarons 11–13, representing a strongly coupled state between the hole and a plasmon 11–12. In many cases, these have been identified as spurious artifacts of the theory applied 13–14, while the dressed hole is in reality accompanied by independent plasmonic excitations 13–19. The lowest valence orbitals of a molecule (i.e. high ionization potential) can similarly deviate from SQP behavior 20–22. To the best of our knowledge, the MQP regime in finite systems has not been studied up to now.

To elucidate the physics of the SQP and MQP regimes, we investigate PES of selected closed shell molecules (NH$_3$, H$_2$O, CH$_4$, C$_2$H$_2$, and N$_2$) using complementary theoretical approaches. Recent methodological developments allow us to access virtually-exact spectra, using the adaptive sampling configuration interaction (ASCI) approach. This reveals a rich MQP character to the spectra, hitherto unexplored with fully correlated methods. We complement our study with physically motivated many-body perturbation theory (MBPT), in the form of GW and vertex corrected GWT. These conceptual approaches enable us to identify the necessary physical ingredients that generate the MQP response, namely the QP-QP interactions that are recovered by the vertex correction.

The physical observable corresponding to the PES is the spectral function $A(\omega)$, which is the trace over the imaginary part of the Green’s function $G_{i,j}(\omega)$, i.e., $A(\omega) = -\frac{1}{\pi} \text{tr} \text{Im} G(\omega)$. The $i,j$ sub-indices correspond to a chosen single particle basis. The physical nature of the peaks in $A(\omega)$ can be assigned by writing the diagonal terms of $G$ in their spectral representation 23. For the hole component, this follows

$$G_{i,i}(\omega) = \sum_m \frac{|\langle \Psi^{N-1}_{m} | c_i | \Psi^{N-1}_{0} \rangle|^2}{\omega + (E^{N-1}_{m} - E^{N}_{0}) - i\eta}, \quad (1)$$

where $|\Psi^{N}_{m}\rangle$ is the $m$-th eigenstate of the $N$ particle system, with energy $E^{N}_{m}$, $c_i$ is the $i$-th annihilation operator and $\eta$ is an integrating factor. From Eq. (1), it can be shown that the peaks in $A(\omega)$ derive from transitions between the $N$ and $N-1$ particle sectors, for which there is a non-vanishing overlap $|\langle \Psi^{N-1}_{m} | c_i | \Psi^{N-1}_{0} \rangle|^2$. In the mean-
FIG. 1: Upper panels: Spectral functions for CH$_4$, NH$_3$ and H$_2$O as computed with ASCI (filled curve), $G_0W_0$ (dot-dashed line) and $G_0W_0\Gamma$ (solid line). Note that the inset in the central panel is in log scale. We mark the SQP and MQP regimes explicitly for H$_2$O. Lower panels: Corresponding real part of the diagonal self-energy terms from $G_0W_0$ and $G_0W_0\Gamma$, one curve per orbital numbered starting with I for the HOMO, shifted by corresponding Hartree-Fock QP energy $\epsilon_0^i$. Symmetry induced degeneracies reduce the number of peaks and self-energy curves in CH$_4$ and NH$_3$. The former has a three-fold degenerate HOMO at $\sim-14$ eV, and the latter a two-fold degenerate at $\sim-17$ eV. The vertical dashed lines mark the position of the ASCI QP energies, and the blue dashed line corresponds to the frequency line $y(\omega) = \omega$. The intercepts of the self-energy curves with the blue dashed line correspond to graphical solutions of the QP equation (2). The arrows point at the features in the $G_0W_0$ highest energy curve which create maxima in the spectral function, see text for discussion.

In practice, we evaluate Eq. (1) via the ASCI algorithm [24–28]. The approach is numerically exact within the basis set chosen; it naturally captures single-QP and multi-QP regimes, regardless of the degree of correlation of the excited states. The spectral features calculated from Eq. (1) represent a series of infinitely sharp peaks, but these may be broadened by coupling to a continuum of states, e.g., to scattering states. Here, we use finite atomic basis sets and a Hermitian Hamiltonian. Hence, only eigenstates of the $N$ and $N-1$ systems are considered and finite lifetimes of individual excitations are thus neglected. To facilitate comparison with the MBPT results, we artificially broaden our spectrum using the $\eta$ parameter. For the technical details of ASCI, including basis set extrapolation, see Supp. Inf. [29].

A conceptually different approach is to obtain the QP energies from the Dyson equation [10]. This relates the Green’s function of the fully interacting QPs $G_{i,j}(\omega)$ and a reference (mean-field) Green’s function $G_{0,0}(\omega)$, through the self-energy $\Sigma_{i,j}(\omega)$. The poles of $G_{i,j}(\omega)$ are subject to the QP fixed point equation:

$$\epsilon_j = \epsilon_0^j + \text{Re} \left[ \Sigma_{j,j}(\omega = \epsilon_j) \right] + \text{Re} \left[ \Delta_j(\omega = \epsilon_j) \right].$$ (2)

Here $\epsilon_0^j$ is a pole of $G_0$ and $\Delta_j(\omega)$ comprises the coupling due to the off-diagonal elements of $\Sigma_{i,j}(\omega)$. The graphical solution to Eq. (2) is presented for selected systems in the lower panels of Fig. 1. The imaginary part of the self-energy is directly related to the QP lifetime and leads to broadening of the spectral features in $A(\omega)$.

In practice, the self-energy is obtained within MBPT by expansion around the screened Coulomb interaction $W$ [10]. In the SQP regime, $\Sigma(\omega)_{i,j}$ is responsible for shifting the poles of $G$ with respect to $G_0$. For MQPs, the structure of the self-energy is necessarily more complex and, in principle, yields multiple solutions to Eq. (2). To capture such correlated states, $\Sigma(\omega)_{i,j}$ must account for the interactions between the particle-hole pairs and ionized holes (or injected electrons) in the system.

The most general form of the self-energy, GW$\Gamma$, introduces the QP couplings via vertex terms, $\Gamma$, which are directly related to two-particle interaction kernels [10, 30–33]. In practice, the vertex corrections are responsible for exciton formation, as well as for mutual coupling of
MQP interactions [10, 32, 34, 36]. While the computational cost of $\Gamma$ is large [35, 37], a recent stochastic formalism introduced a linear-scaling algorithm, which we apply here [36]. It is far more common to neglect the excitonic and MQP couplings, e.g., as is done in the $GW$ method [35, 39], which includes correlations approximately, as induced time-dependent density fluctuations.

The computed spectral function is illustrated in the top panel of Fig. 1 for the CH$_4$, NH$_3$, and H$_2$O molecules. The distinction between the SQP and MQP regimes is evident from comparing excitations at different energies. In general, both the highest occupied molecular orbital (HOMO) states, which appear at the lowest absolute frequencies, and states energetically close to these are composed of a single sharp peak per orbital, consistent with the SQP picture. In contrast, excitations far away from the HOMO exhibit broader peaks; their spectral intensity is often redistributed to multiple satellite features. This is a signature of the MQP regime. For the first time, we are able to study this behavior in molecules with a fully correlated approach. The question remains whether these satellites represent a weak coupling of, in principle, distinguishable QPs, and to what extent the MQP couplings included by the vertex correction are necessary to describe the spectral functions.

In Fig. 2, we compare the QP energies for all valence excitations in all five molecules obtained with the different methods. This demonstrates the accuracy of the vertex term in comparison to ASCI, which, as expected [30–38, 35, 37], has improved agreement over HF and $GW$. We find the best agreement for the holes of the HOMO states (i.e. the first ionization potentials). These are in the SQP regime, where the self-energy is merely responsible for shifting the poles of the Green’s function and the excitations appear as sharp peaks. However, the presence of the vertex corrections is important, as illustrated in the inset of Fig. 2. The one-shot $GW$ approach performs only slightly better than HF; the mean absolute deviation (MAD) with respect to ASCI is 1 eV and 0.8 eV for HF and $GW$, respectively. Upon inclusion of vertex terms, however, MAD decreases to 0.3 eV. The presence of $\Gamma$ is responsible for the excitonic effects in $W$, and these are likely non-negligible in small systems where electrons and holes have large spatial overlaps. Further, the vertex correction cancels, at least partially, the spurious self-polarization in $GW$ [10, 11]. The latter is likely the major driving force of the improvement, because the electron-hole interactions in the screening tend to have little or (surprisingly) negative impact on the QP energy predictions [35, 36, 42].

While most previous studies limited themselves to the SQP regime around the HOMO state, here we also examine the higher energy excitations, which exhibit MQP behavior. Due to its lack of correlation, the HF ionization potentials deviate significantly from the ASCI QP behavior. Due to its lack of correlation, the HF ionization potentials deviate significantly from the ASCI QP behavior. Due to its lack of correlation, the HF ionization potentials deviate significantly from the ASCI QP behavior. Due to its lack of correlation, the HF ionization potentials deviate significantly from the ASCI QP behavior. Due to its lack of correlation, the HF ionization potentials deviate significantly from the ASCI QP behavior.

FIG. 2: quasiparticle energies (QPE) for the different molecular systems computed from ASCI vs the QPEs computed with the approximate methods. The symbols correspond to: Hartree-Fock (HF, empty), $G_0W_0$ (half-filled), and the vertex corrected $G_0W_0\Gamma$ (solid). The energy region where the excitations present MQP character is shaded yellow. The number of QPEs per molecule is given in the legend. The inset shows the mean average deviation (MAD) between the ASCI results and the three approximations.
three-peak feature responds to the self-energy having a single true pole (middle arrow in lower central panel of Fig. 1), but having two nearby frequencies where Eq. (2) is approximately fulfilled (left and right arrows). In almost all of the molecules, the main maximum corresponds one of these two “pseudo-poles” (rightmost arrow). A similar structure was seen in previous calculations for solids 19, 18, 19. Here, due to the finite real-time propagation employed in our stochastic implementation 35, 33, 34, some of the “pseudo-poles” may correspond to actual poles. Only for N2, does Eq. (2) have two solutions (i.e., two poles). Here the resulting $A(\omega)$ features only a single prominent peak associated with the low-energy QP 29. To summarize, ASCI shows a complex satellite structure, whereas GW only presents this regular three-peak spectral feature.

Qualitatively, the existence of multiple solutions in closed shell systems is consistent with a hypothetical “plasmaron” QP, representing a resonantly bound hole and a collective neutral excitation. In solids, this was interpreted as an electron-plasmon state. However, as noted above, it was eventually identified as an artifact of GW 8. In practice, the GW approximation spuriously substitutes the multiple satellite structure with a single secondary QP that does not correspond to a true excited state. Nevertheless, for weakly interacting MQPs, the absence of satellites can be remedied by reconstructing the Green’s function (and $A(\omega)$) via the cumulant expansion technique 19, 35. This method reproduces the multiple peak structure, but it inherently assumes the presence of a distinguishable neutral excitation, which corresponds to a pole of $W$ dominating the electrodynamic screening. This in turn implies that $|\Psi_m^{-1}\rangle$ in Eq. (1) has an entangled direct product structure, with the total energy being additive in the hole and neutral excitation energies. The reconstructed $A(\omega)$ exhibits then a regular satellite structure, in which peaks appear at energies corresponding to the multiples of the plasmon energy. Conceptually, the $n$-th satellite maximum represents the energy of a single hole plus $n$ excited plasmons. The weak coupling regime is justified for localized holes in the presence of delocalized neutral excitations 8. However, this separation is hard to conceive in small finite systems and cannot be readily justified for molecules. Furthermore, the fully correlated ASCI results do not exhibit a regular pattern of satellite peaks, suggesting that the MQP regime comprises at least some entangled $|\Psi_m^{-1}\rangle$ states.

In contrast to GW, the vertex correction in GWT recovers the inter-orbital interaction that enables mutual coupling between holes and neutral excitations. In theory, this should be enough to describe the MQP regime. Indeed, the GWT yields multiple peaks in the spectral function, beyond the three-peak artifact structure observed in GW and instead recovering the same kind of rich satellite structure present in the ASCI spectra. The vertex corrected self-energy is illustrated for CH4, NH3 and H2O in Fig. 1. Clearly, it exhibits a more complex frequency dependence compared to the GW result. For all systems, we observe that spectral features of the self-energy $\Sigma$ are strongly enhanced for the highest energy states and that GWT has multiple solutions to Eq. (2). For NH3 in particular (inset in Fig. 1), the double peak in the $\sim 30$ eV region is accompanied by small satellites at lower energies stemming from the variation of the self-energy, which seem to match many of the features in ASCI.

The distant satellites are not true poles, but instead appear due to the combination of small denominator in Eq. (1) with the small imaginary part of the self-energy. Possibly, and at least in part, this is caused by numerical broadening due to the finite real-time propagation. Nevertheless, the highest energy states of H2O and N2 are at much lower energies and exhibit even stronger oscillations. For these excitations, we observe a plethora of poles (more than ten) with energies almost 30 eV below the main QP peak (see Fig. 1 and 29). Note that the effect of the vertex is possibly overestimated due to the absence of self-consistency. The self-consistent solution contains screened Coulomb interactions in $\Gamma$ 30, 33. This renormalization will weaken the MQP couplings, reducing the oscillatory behavior shown in H2O and N2, retaining the envelope of their $A(\omega)$ and resulting in a smooth behavior, like for the other molecules.

As a final point, another manifestation of the MQP regime is a mixed orbital character of the orbital resolved spectrum $A(\omega)_i = -\frac{1}{\pi} \text{Im} [G_{ii}(\omega)]$. In a natural orbital basis, the ASCI $A(\omega)_i$ for the valence state furthest away from the HOMO features additional peaks at a frequency corresponding to another excitation 29. Note that $A_i(\omega)$ is subject to the choice of single-particle basis, and therefore this seems a priori to be a statement about the composition of the natural orbitals. Remarkably, however, the GWT self-energy captures these resonances as well. The vertex corrected self-energy of the highest energy state in Fig. 1 shows a strong resonance at $-11$ eV (i.e., 16 eV above the QP energy), coinciding with the HOMO QPE. Similar features are found for all the molecules with the exception of CH4, and are further enhanced for the highest energy states of H2O and N2, leading in the latter case to an additional QP pole 29. The presence of character mixing in both the ASCI and GWT spectral functions $A(\omega)$ further underlines the importance vertex term to capture complex PES features.

From our results, it is clear that the MBPT self-energy offers a useful diagnostic tool to identify the strength of the QP-QP coupling. It can distinguish between true Green’s function poles, akin to the plasmaronic state, and “pseudo-poles”, coming from weakly coupled excitations, i.e., from what are effectively product states. The one-shot vertex correction recovers the QP interactions needed for both kinds of spectral features, so that upon renormalization GWT will provide an invaluable tool to disentangle the excited state wave function structure. We note that beyond this kind of numerical theoretical analysis, the coupling strength should be accessible experimentally, e.g., by measuring the lifetime changes of opti-
cal transitions due to simultaneous ionization of the system [47].

Understanding the photo-emission spectra of many-body systems requires the accurate description of both single-quasiparticle and multi-quasiparticle regimes. We contribute to this long standing issue by providing virtually-exact photo-emission spectra for small molecular systems. These unveil a rich satellite structure of bottom valence spectra, and allows us to inform the development of many-body perturbation theory methods, in particular those beyond GW. We investigate whether the addition of vertex corrections recovers the satellite structure reliably, something which has been long assumed in the many-body literature. We show that including the vertex improves quasiparticle energies across all energy scales, and also introduces additional features in the self-energy which translate to a rich satellite structure. The nature of the excited states that these satellites correspond to remains an open question, which may be answered theoretically or experimentally. On the theory side, we identify the lack of screening in the exchange interaction as the foremost problem in the current GWT implementation. Our results should encourage the further development in vertex corrected MBPT approaches. Beyond small molecular systems, this will have a decisive effect on the path towards fully ab initio description of quantum materials.

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