Hydrogen molecule spectrum by many-body GW and Bethe-Salpeter equation

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(Dated: October 16, 2020)

We check the \textit{ab initio} GW approximation and Bethe-Salpeter equation (BSE) many-body methodology against the exact solution benchmark of the hydrogen molecule $\text{H}_2$ excitation spectrum and in comparison with configuration interaction (CI) and time-dependent Hartree-Fock. The comparison is made on all the states we could unambiguously identify from the excitonic wavefunctions’ symmetry. At the equilibrium distance $R = 1.4 a_0$, the GW+BSE energy levels are in good agreement with the exact results, with an accuracy of 0.1–0.2 eV. GW+BSE potential-energy curves are also in good agreement with the CI and the exact result up to 2.3 $a_0$. The solution does not exist anymore beyond 3.0 $a_0$ for triplets (4.3 $a_0$ for singlets) due to instability of the ground state. We tried to improve the GW reference ground state by a renormalized random-phase approximation (r-RPA), but this did not solve the problem.

Hydrogen $\text{H}_2$ is the simplest neutral molecule and one of the most straightforward many-body systems in nature. In contrast to the hydrogen atom, where the exact analytical solution is known, $\text{H}_2$ already faces the quantum many-body problem to calculate electronic correlations. Due to the presence of two electrons and their many-body interaction, the closed-form solution of the Schrödinger equation for $\text{H}_2$ does not exist. Nevertheless, thanks to James and Coolidge’s pioneer work \cite{1}, the methodology devised originally by Hylleraas \cite{2} for the helium atom, which provides an exact solution in a numerical analysis sense, was adapted to $\text{H}_2$. By exploiting the rotational symmetry around the dimer axis, the $\text{H}_2$ wavefunction can be written as a power series of five coordinates (instead of the three helium Hylleraas coordinates), that is the elliptic confocal coordinates $\xi_1, \xi_2, \eta_1, \eta_2$ and the electrons distance $\rho$. In analogy with the hydrogen and the helium atom, also for $\text{H}_2$ an exponential on the elliptic radial coordinates $\xi_1$ and $\xi_2$ is introduced to speed up the series convergence. The solution is then searched by varying the series coefficients up to a given order. Meanwhile, the next order can be used to evaluate the absolute error. By increasing the order of the series, the error can be arbitrarily reduced. Today the $\text{H}_2$ solution is known up to an accuracy of $10^{-12}$ \cite{3}. Beyond to provide a rigorous way to validate theory against more and more accurate experiments \cite{4, 5}, this exact numerical result makes $\text{H}_2$ an ideal workbench to check any approximate many-body methodology.

In this work, we use the $\text{H}_2$ exact solution benchmark to check the \textit{ab initio} many-body methodology of the GW approximation on the self-energy and the resolution of the Bethe-Salpeter equation (BSE) \cite{6}. To this purpose, the comparison is done against the exact solution of the idealized non-relativistic and clamped nuclei $\text{H}_2$ Hamiltonian, excluding nuclear motion, relativistic and QED radiative corrections and other complications not related to the many-body problem to calculate correlation energies. We also compare with other more or less accurate many-body approaches, from full configuration interaction (CI) \cite{7} down to Hartree-Fock (HF), passing through time-dependent HF [TDHF, also known in nuclear physics as random-phase approximation (RPA) \cite{8}, or RPA with exchange diagrams (RPAX)], and finally an approach known as renormalized RPA (r-RPA) \cite{9, 10, 11, 12}. The comparison is made on all the states it was possible to identify. Our results show that at the $\text{H}_2$ equilibrium distance of $R = 1.4 a_0$, the GW+BSE energy levels are in good agreement with the exact results, with an accuracy of 0.1–0.2 eV, four times better than TDHF. The GW+BSE energy-potential curves as a function of the nuclei distance are also remarkable up to at least $R = 2.3 a_0$, after where they start to deteriorate. Beyond $R = 3.0 a_0$ we have no more GW+BSE solutions due to ground state instability. This problem is not solved by r-RPA.

The starting point of our \textit{ab initio} many-body calculation is a standard HF calculation. One can also start from density-functional theory (DFT), e.g. in the local-density approximation or else, but we opted for the zero-correlation more meaningful physical HF for our comparisons. This is also the most standard for isolated systems. We used a $d$-aug-cc-pV5Z \cite{14} correlation-consistent Gaussian basis set with angular momentum up to $l = 5$ and a double set of diffuse orbitals for all our calculations. On top of HF we performed a GW self-energy contour-deformation calculation with self-consistency only on quasiparticle energies using a Coulomb-fitting resolution of the identity (RI-V) with the associated auxiliary basis $d$-aug-cc-pV5Z-RI \cite{15}. The last step was a BSE calculation beyond the Tamm-Dancoff approximation of the excitation energies $\Omega_\lambda$ and the excitonic wavefunctions $\Psi_\lambda$ by diagonalization of the excitonic Hamiltonian

$$
\begin{pmatrix}
A & B \\
-A^* & -B^*
\end{pmatrix}
\Psi_\lambda = \Omega_\lambda \Psi_\lambda,
$$

(1)
where \( \phi \) are Coulomb interaction matrix elements between \( w \) quasiparticle energies, and are indicated as small dots and their axis is oriented along electron distribution: on the right in red; electron distribution: on the right in blue. The two H atoms are indicated as small dots and their axis is oriented along \( z \).

\[
A = (\epsilon_p - \epsilon_h)\delta_{pp'}\delta_{hh'} + w_{ph'}h' - W_{ph'h},
\]
\[
B = +w_{pp'h'h} - W_{pp'h'h},
\]

where \( \epsilon_h/\epsilon_p \) are hole/particle (occupied/empty) \( GW \) quasiparticle energies, and \( w/W \) are bare/screened Coulomb interaction matrix elements between \( GW \) states \( \phi_i \), e.g. \( w_{ij} = \langle \phi_i(r) \phi_j(r') | w(r, r') | \phi_k(r) \phi_l(r') \rangle \). The ground state energy was calculated by the formula \( 16 \)

\[
E_0 = E_0^{\text{HF}} + \frac{1}{2} \left( \sum_{\lambda} \Omega_{\lambda} - \text{Tr}(A) \right) .
\]

We used the codes NWChem \( 17 \) and ORCA \( 18 \) for HF and CI calculations, and Fiesta \( 19 \) \( 20 \) with some checks by TurboMole \( 22 \) for \( GW \), BSE, r-RPA and TDHF.

In Fig. 1 we plot the excitonic wavefunctions \( \Psi_\lambda \) of the most intuitive excitons. At the left and in red we plot the hole distribution, \( \rho_h (r_h) = \int dr \Psi_\lambda^2 (r_h, r) \), trivially the 1s-like orbital of the ground state, and at the right and in blue the electron distribution \( \rho_e (r_e) = \int dr \Psi_\lambda^2 (r_h, r_e) \) in the planes \( xz \), \( yz \) and \( xy \). Study of the symmetry of the excitonic wavefunctions is essential to the unambiguous identification of the orbitals of the \( \text{H}_2 \) molecule, including the less intuitive ones, to compare with the literature.

In Fig. 2 and in Table I we report the \( \text{H}_2 \) ground and excited state energy levels. To identify the states, we use the notation by Dieke \( 23 \), and we also indicate the united atoms (He) notation used by Sharp \( 24 \). We report the exact levels from literature \( 25 \) \( 29 \) which, n.b., are the solution to the clamped nuclei (at the equilibrium distance \( R = 1.4 a_0 = 0.74 \, \text{Å} \) \( \text{H}_2 \) non-relativistic Schrödinger equation. High accuracy comparisons with the experiment should also consider nuclear motion, relativistic, and QED corrections \( 4 \) \( 3 \). We then report our TDHF, \( GW+BSE \), and CI results, all calculated at the same \( d_{-2}^{\text{aug}}-cc-pV5Z \) basis level. Full CI has a remarkable accuracy of \( 4 \cdot 10^{-4} \, \text{Ha} \), at least up to the \( h \) state, beyond which the performances of the \( d_{-2}^{\text{aug}}-cc-pV5Z \) basis start to deteriorate, and the error raises one order of magnitude \( 5 \cdot 10^{-3} \, \text{Ha} \). The latter is rather the accuracy of the \( GW+BSE \) results since the ground state. There are some more favorable cases, like the states \( b, h \) and in particular \( C \), where the performances seem even better than CI. But this is due to the fact that the exact result in literature \( 25 \) is absent at the equilibrium distance \( R = 1.4 a_0 \) and quoted only for \( R = 1.375 a_0 \). Our calculation at \( R = 0.73 \, \text{Å} = 1.379 a_0 \) provided \( E = -0.6855 \) for CI and \(-0.6811 \, \text{Ha} \) for \( GW+BSE \) which restablishes the correct order of accuracy between methods. For the other states, the better agreement of \( GW+BSE \) should be considered fortuitous, and the absolute error can be quantified at the level of \( 0.1 \sim 0.2 \, \text{eV} \), thus confirming previous estimates for the \( GW \) approximation. This is not at all bad if we compare with the absolute error of \( 0.5 \, \text{eV} \).
that we can estimate for TDHF. So the route of introducing correlations on top of HF by introducing screening, the screened Coulomb interaction $W_\lambda$, both at the level of the self-energy in the GW step and in the BSE kernel, once again proves as an improvement over the simpler unscreened TDHF (RPAx).

In Fig. 3 we plot the energy as a function of the internuclear distance for all the states of Table I plus others for which we could find further data in the literature. We again compare the GW+BSE curve to the CI and the exact result (the experiment for the $B'$ and $e$ states for which we could not find exact calculations in literature). The agreement with both CI and the exact result can be considered very good, at least up to $R = 2.3 a_0$. This is more than sufficient to capture the relevant range of the molecule binding. Then it starts to deteriorate, and after $R = 3.0 a_0$, we have no more GW+BSE solution. From this point on, a triplet instability occurs: the diagonalization of the Bethe-Salpeter excitonic matrix provides imaginary eigenvalues, signaling that the reference ground state, the GW one calculated (non fully self-consistently with respect to the wavefunctions) on top of the HF, is unstable toward another lesser energy ground state. We can see in Fig. 3 that the unbound triplet b $3\Sigma^+_u$ state, at the last point beyond $3 a_0$, takes the value of $-1.01 \text{ Ha}$, implying that it has already unphysically crossed the asymptote of $-1.0 \text{ Ha} = -2.0 \text{ Ryd}$ which is the exact analytic energy of two dissociated H atoms. After that distance, the GW+BSE b $3\Sigma^+_u$ state tends to swap with the true ground state X $1\Sigma^+_g$ and to become a spurious ground state with total spin $S = 1$. For singlets, the instability occurs a bit further away, at $R = 4.3 a_0$, so that the agreement with the CI and exact results lasts a bit longer. This would be even more evident if we compare excitation energy-differences with respect to the ground state, i.e. directly the $\Omega_\lambda$ out of Eq. (1), instead as the absolute excitation energies of the exact $\Omega_\lambda$ and orbitals $\phi_i$ better than the GW or HF. A possibility can be the renormalized RPA (r-RPA) approach described in Ref. [9.12]. Compared to non fully self-consistent GW, which updates only quasiparticle energies, r-RPA updates both energies and occupation numbers. Such effect introduces some correlation on top of HF wavefunctions, so to have a better ground state and in the hope of pushing the instability to larger distances. In principle, r-RPA should be carried up to self-consistency, typically 3 or 4 iterations. Here we only did a single iteration to see whether there is already an improvement on TDHF/RPAx and the HF reference ground state. In Fig. 3 we report the results only for the ground state. We first plot the HF uncorrelated result and the unrestricted HF (UHF), which coincides with restricted spin $S = 0 \text{ HF}$ up to the Coulson-Fisher point at $2.3 a_0$. We then report the GW+BSE result, which at the equilibrium distance is at $0.1\sim 0.2 \text{ eV}$ from the exact and the CI result. The GW+BSE solution does not exist anymore beyond $3 a_0$ (triplet instability), with problems starting already at $2.8 a_0$. For the TDHF (RPAx) ap-

| state | TDHF $GW+BSE$ | CI | Exact [Ha] |
|-------|---------------|----|------------|
| X $3\Sigma^+_g$ | 1sσ | -1.19 | -1.181 | -1.1742 |
| b $3\Sigma^+_u$ | 2pσ | -0.82 | -0.783 | -0.7838 |
| a $3\Sigma^+_g$ | 2sσ | -0.73 | -0.717 | -0.7133 |
| c $\Pi_3$ | 2π | -0.72 | -0.710 | -0.7062 |
| B $3\Sigma^+_g$ | 2pσ | -0.71 | -0.698 | -0.7054 |
| C $\Pi_3$ | 2pπ | -0.69 | -0.684 | -0.6882 |
| h $3\Sigma^+_u$ | 3sσ | -0.64 | -0.631 | -0.6299 |
| i $\Pi_3$ | 3dπ | -0.63 | -0.622 | -0.6218 |
| I $\Pi_3$ | 3dπ | -0.63 | -0.622 | -0.6217 |
| g $3\Sigma^+_u$ | 3dσ | -0.63 | -0.622 | -0.6206 |
| m $3\Sigma^+_u$ | 4fσ | -0.61 | -0.604 | -0.6055 |

$^a$ The exact [25] result for the C state refers to $R = 1.375 a_0$. TABLE I. H$_2$ energy levels [Ha] at the equilibrium distance $R = 1.4 a_0$. We compare TDHF (RPAx), GW+BSE and CI results, all calculated at the d-aug-cc-pV5Z basis, to exact results in literature: X, b, C [25], h, g [26], a, B [27], c, i, I [26], m [30].
The result, as shown in Fig. 4, is not that bad. The RPA+BSE approach, problems start already at 2.1 \( a_0 \), with no more solution (triplet instability) after 2.3 \( a_0 \). We can say that the problem is more severe in TDHF/RPAx than in GW+BSE, though for GW+BSE, a singlet instability appears after 4.3 \( a_0 \), whereas there is no singlet instability at any distance for TDHF. On the other hand, there is no instability problem at all for the (direct) RPA calculation on top of HF (HF+dRPA): there is no singlet instability in dRPA, like in RPAx, while triplets energies keep at the uncorrelated level of HF energy differences in dRPA, so that they do not contribute to the ground state correlation energy. The HF+dRPA improves the HF curve, but the dissociation limit (not shown, see e.g. Ref. 33) is still too large. Finally, we report our r-RPA result above, and so better than TDHF/RPAx, almost achieving the same accuracy of GW+BSE. But also for r-RPA, the solution does not exist beyond 2.3 \( a_0 \); on this point, r-RPA does not improve on TDHF/RPAx. We can consider the GW+BSE reference ground state still better, even though in this approach we only update quasiparticle energies and not also the wavefunctions, like in r-RPA. To clarify this point, we performed a hybrid r-RPA+BSE calculation consisting in the use of the r-RPA approach to update both energies and also occupation numbers and wavefunctions, together with the use of the BSE \( w-W \) kernel with the screened Coulomb interaction \( W \), instead of the bare Coulomb \( w \) of TDHF/RPAx and of the simplified r-RPA approach which does not update the kernel shape. The result, as shown in Fig. 4, is not that bad. r-RPA+BSE improves the agreement with the exact result at the equilibrium distance, and the triplet instability occurs at almost the same distance of the GW+BSE approach. In principle, in full self-consistent RPA (SCRPA) calculations beyond simplified r-RPA, the kernel is also updated and should start to contain screening. Nevertheless, the hybrid r-RPA+BSE is not very well justified from an analytic perspective. We also observe that the hybrid curve manifests a strange crossing with the exact results curve, which looks quite unphysical.

To the best of our search in the literature, we could only find the results of Ref. 35 as relevant for our study of \( \text{H}_2 \) excitations. Their results refer to a minimal basis set and cannot be directly compared to the real experimental/exact \( \text{H}_2 \). Nevertheless, our and their results are coherent qualitatively (see their Fig. 1 by non-exact \( G_0 \)). On the \( \text{H}_2 \) ground state the literature is vaster. Our HF+dRPA curve practically coincides with the RPA@HF curve of Ref. 35, though we used the trace formula (TF) Eq. (2) and they used the adiabatic-connection fluctuation-dissipation theorem (ACFDT) \( \lambda \)-integration. This confirms that the two formulas are equivalent in the direct RPA case, as demonstrated 37. In the other cases, i.e. TDHF/RPAx or GW+BSE, the two formulas are not equivalent, and their results may differ. Thus the TDHF curve by ACFDT, called HF-RPA in Ref. 38, differs from our TDHF by TF 39. Triplets are included in the TF Eq. (2), whereas they do not contribute to ACFDT TDHF, resulting in larger energy. On the other hand, the advantage is the absence of the triplet instability problem; in TDHF ACFDT the solution exists up to dissociation. ACFDT should be in trouble for GW+BSE where the instability also occurs for singlets. In Ref. 10, they took into account only the \( R \) and the \( \lambda \) where a real solution exists for singlets, and neglect all imaginary poles. Although our GW+BSE correlation energy by TF is more accurate at the equilibrium distance, their approximation revealed successful in describing the dissociation limit. This strategy cannot evidently help here where we are interested in excited states.

In conclusion, on the benchmark of the \( \text{H}_2 \) exact result, the GW+BSE many-body approach achieves at the equilibrium distance an accuracy of 0.1~0.2 eV, four times better than the TDHF (RPAx) 0.5 eV error, on all the states up to \( m \Sigma^+_G 4\sigma \). GW+BSE energy-potential curves are in good agreement with CI and exact results at least up to 2.3 \( a_0 \) and stop at the triplet instability at 3 \( a_0 \). Improvement of the GW reference ground state by the r-RPA approximation, which updates not only energies but also occupation numbers and wavefunctions, does not improve on the triplet instability problem. The introduction of screening in r-RPA, as by an r-RPA+BSE hybrid, improves the triplet instability, which occurs at a similar distance comparing to GW+BSE.

We thank X. Blase, I. Duchemin, and P. Schuck for useful discussions.

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