Precise computation of rovibronic resonances of molecular hydrogen: \( EF^{1}\Sigma^+_g \) inner-well rotational states

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Abstract

Selected states of the \( EF^{1}\Sigma^+_g \) electronic manifold of the hydrogen molecule are computed as resonances of the four-body problem. Systematic improvement of the basis representation for the variational treatment is achieved through an energy-tracking optimization procedure. The resulting non-relativistic energy is converged within 1 \( nE_h \), while the predissociative width is found to be negligible at this level accuracy. The four-particle non-relativistic energies are appended with relativistic and radiative corrections which close the gap between the experimental observations and earlier theoretical work.
The lowest-energy rotational and vibrational states of the ground electronic state of the hydrogen molecule have received much attention over the past decade. We have witnessed several orders of magnitude improvement in terms of accuracy and precision both on this experimental [1–4] and theoretical [5, 6] frontier of molecular physics.

The hydrogen molecule has several electronically excited states, many of them are very interesting by their own, e.g., the famous double-well features caused by avoided crossings. The rovibronic level structure is dominated by strong and less strong non-adiabatic interactions among the states, not yet fully, quantitatively understood. In the meanwhile, many of these electronically excited states have been measured experimentally to high precision [3, 7], and rovibronic states corresponding to electronic excitations, e.g., the $E F$ and $G K \ 1\Sigma_g^+$ manifolds, have been used in the excitation sequences resulting in the ultra-precise dissociation energy of the lowest rovibrational levels of the ground electronic state [2–4]. Therefore, it is not only for purely theoretical interest to aim for a better and more complete theoretical description of electronically excited states of the hydrogen molecule. In particular, the entire dynamical range of molecular hydrogen, which has already been experimentally studied, spans an about 130 000 cm$^{-1}$ broad energetic and a 15 bohr broad structural (proton-proton separation) range, and includes a very large number of sharp spectral transitions which can be measured to high precision. For this reason, we think that the computation of a variety of these rovibronic states would offer an excellent testing ground for the numerous small (or often not so small) ‘effects’ which have been identified during the study of the ground state of H$_2$, see for example, Ref. [6]. The present work cannot aim for including all these effects at once, but we wish to provide a good starting point by significantly improving upon earlier theory for the selected states.

H$_2$ has several, challenging excited states, some of them are bound even in the four-body treatment, e.g., the rovibronic levels of $B \ 1\Sigma_u^+$. In the present work, we will look at the first electronically excited state beyond the ground state, which is the $E F \ 1\Sigma_g^+$ state. The Born–Oppenheimer (BO) potential energy curve of $E F \ 1\Sigma_g^+$ shows the notorious double-well feature due to an avoided crossing with the nearby $G K \ 1\Sigma_g^+$ state (Figure1). In a pre-Born–Oppenheimer (pre-BO) description [8–10],
‘all’ non-adiabatic couplings and ‘effects’ are automatically included, so we will not use potential energy curves, nor coupling vectors in the computations, but the curves are useful to look at and we will continue to use the electronic state labels to have a short description and reference for the computed four-particle states. Since all non-adiabatic couplings are included, also the coupling with the $X \, 1\Sigma^+_g$ (ground) state is present (we cannot separate it), and thus the $EF$ states can only be obtained as resonances within the four-body problem [9]. The lower-energy vibrations of $EF$ have been estimated to have a very long predissociative lifetime (much longer than their radiative lifetime) due to their very weak coupling to the dissociation continuum of the $X \, 1\Sigma^+_g$ ground electronic state [9, 11].

The non-adiabatic manifold, which includes also the $EF$ state, was computed by Yu and Dressler [12] by explicitly coupling nine electronic states. Yu and Dressler used accurate potential energy curves and non-adiabatic coupling vectors, and their nine-state computation resulted in rovibronic term values within 0.1–20 cm$^{-1}$ of experiment. This nine-state computation was a significant improvement upon the earlier five-state study of Quadrelli, Dressler, and Wolniewicz [11], which showed a larger, 1.3–120 cm$^{-1}$ deviation from the experimental results. As it was pointed out by Hölsch, Beyer, and Merkt [7] recently, performing a non-adiabatic computation with more than nine fully coupled electronic states for this system is not obvious but extension of non-adiabatic perturbation theory could be possible. The effective Hamiltonian for the quantum nuclear motion over coupled electronic states which perturbatively accounts for the effect of the distant electronic states (not included in the fully coupled electronic band) has been recently formulated [13] and its numerical application, by generalizing the computational approach developed for a single-state non-adiabatic Hamiltonian [14, 17], should soon follow.

However, benchmark energies and wave functions are best obtained from the direct solution of the four-particle Schrödinger equation. Some time ago [9], we have identified rovibronic resonances in pre-BO computations, also from the $EF$ manifold, by using symmetry-adapted, explicitly correlated Gaussian (ECG) basis functions optimized for bound states. The global-vector representation [18, 19] of ECGs made it possible to have a general basis set for $N \geq 0$ total angular momentum quantum number. At that time, a systematic improvement of the basis representation for
resonances was not available, which made it difficult to assess the accuracy of the results. Although a complex analogue of the real variational principle is available for the complex-coordinate rotated (CCR) Hamiltonian \[20\], the practical utilization of this complex variational principle for basis function optimization is not straightforward (of course, its utility for computing the energy and the width for a given basis set is well-established). In this work, we propose a practical approach inspired by the stabilization method \[20–22\], which will be useful for the systematic improvement of the basis set for long-lived resonance states that are only weakly coupled to the continuum.

It is well known that basis functions can be optimized for the \(n\)th excited bound state by minimizing the \(n\)th eigenvalue of the Hamiltonian matrix \[18, 23\]. If we used this procedure to minimize the energy of a resonance (by picking the \(n\)th eigenstate in a starting basis set, which is beyond the dissociation threshold and resembles most the resonance to be computed) then, after a few basis refinement cycles, discrete representations of the continuum would start to accumulate in our energy list and we would end up minimizing the energy converging to the dissociation threshold. In order to avoid this minimization ‘collapse’, we do not focus on the \(n\)th state but we define an energy threshold, \(\varepsilon\), the energy of which is slightly smaller than the exact energy of the state we are looking for. (This value can be estimated and does not need to be a very tight estimate; in practice we use the experimental term to set a loose lower bound). We use this ‘energy-tracking’ procedure to optimize the basis representation for the selected rovibronic state by minimizing the energy of the first state above the \(\varepsilon\) energy threshold. It is important to add that the energy tracking (in its simplest form) works for long-lived resonances, which couple to the continuum only weakly, and the energy of which in increasing but finite basis sets stabilizes over many iteration cycles. During the refinement cycles, discrete representations of the continuum may drop in our energy list, but we track and minimize the energy of that state which is the lowest above our \(\varepsilon\) threshold. We use this procedure only to optimize the basis functions. Following the basis optimization, resonance features can be studied by the complex-coordinate rotation (CCR) technique \[20\], as it was implemented for the pre-BO problem in Ref. \[9\]. The point at which the CCR trajectories stabilize on the complex energy plane will define the full (complex)
molecular wave function of the resonance (the complex energy and the CCR angle). This complex wave function can then be used to compute relativistic and radiative corrections, using the CCR form of these operators, to obtain the relativistic and radiative corrections for both the energy and the width (lifetime) [24].

Now, we focus our attention to the computation of the rotational excitations, with $N = 0, 1, 2, 3, 4,$ and 5 total angular momentum quantum numbers, of the lowest-energy vibration in the inner well of the $EF \, ^1\Sigma^+_g$ electronic state. The inner-well ground vibrational state is usually labelled with $E_0$ [12], so we will use $E_0 N$ for the $N$th rotational excitation of this state. We can access these states by choosing the appropriate non-relativistic quantum numbers, which are listed in caption to Table I, and by defining the $\epsilon$ energy threshold for the energy-tracking procedure, which we set to ca. 10–20 cm$^{-1}$ lower than the energy estimated from the experimental term value. Using the QUANTEN computer program [8–10], we optimized, in repeated refinement cycles, a starting basis set which was compiled from the extensive bound-state optimization work of Ref. [9]. In retrospect, we can confirm that the largest basis set of Ref. [9] gives $EF$ energies accurate within ca. 10 nE$_h$, which we can estimate now from the convergence pattern and behaviour of the states upon the systematic refinement of the basis set.

In Table II, we list the non-relativistic energy values optimized in the present work ($E_{nr}^{(2)}$ column), which are estimated to be within $\sim$ 1 nE$_h$ of the exact, non-relativistic value. The non-relativistic term values, the difference of the $E_0 N$ energies and the non-relativistic energy of the ground state ($X_{00}$), reduce the 0.3 cm$^{-1}$ deviation of the nine-state non-adiabatic computation of Yu and Dressler [12] to 0.1 cm$^{-1}$, and confirm their error estimates. Yu and Dressler also estimated the relativistic and radiative corrections to be ca. 0.08 cm$^{-1}$ for the $E_0 N$–$X_{00}$ terms. This is an average value for the states with different rotational quantum numbers, and was compiled from the expectation value of the Breit–Pauli Hamiltonian with the electronic wave function at $R = 1.9$ bohr [25] and the radiative correction of $H_2^+$ [26] at the $R = 1.9$ bohr proton-proton distance, which is near the effective structure of the $E_{00}$ state. If we correct our non-relativistic term values with this estimate, then the deviation from experiment reduces to (0.035, 0.036, 0.040, 0.045, 0.050, 0.057) cm$^{-1}$ for the $N = 0, 1, 2, \ldots, 5$, respectively.
We would like to have a more complete account for the relativistic and radiative effects and also to possibly know the $N$ dependence of the correction. For this purpose, we performed the following calculations using the non-relativistic, pre-BO wave function, compiled data from the literature and carried out a few additional computations (partly to test the convergence of the literature data). The relativistic, radiative, and higher-order radiative effects (we have explicitly considered estimates up to the so-called $\alpha^7$ terms) is calculated as perturbative corrections using the non-relativistic energy and wave function, $E^{(2)}$ and $\psi$, in terms of increasing orders of the fine-structure constant, $\alpha$,

$$E^{(2+7)} = E^{(2)} + \sum_{k=2}^{5} \alpha^k \langle \psi | H^{(k+2)} | \psi \rangle$$

where the $H^{(k+2)}$ Hamiltonians are reproduced in the following paragraphs with the usual meaning of the symbols and operators (the details can be found in the references).

To calculate the (spin-independent) relativistic correction, we have started out from the expectation value of the Breit–Pauli Hamiltonian (of the electrons) \[27, 28\]

$$H^{(4)} = -\frac{1}{8}(\nabla_1^4 + \nabla_2^4) + \frac{\pi}{2} \sum_{i=1}^{2} \sum_{a=1}^{2} \delta(r_{ia})$$

$$- \pi \delta(r_{12}) + \frac{1}{2} r_{12}^{-1} [\nabla_1 \nabla_2 + r_{12}^{-2} (r_{12} \nabla_1 \nabla_2) \nabla_2].$$

Wolniewicz already calculated the expectation value of $H^{(4)}$ with the electronic wave function along a series of nuclear configurations. We obtained the relativistic correction to each $E0N$ state by evaluating the expectation value of the BO relativistic correction curve (represented with polynomial fits) with the pre-BO wave functions. To obtain the term corrections, $\delta T_{rel}^{(4)}$ (Table II), we used the relativistic correction value, $-1.652 \text{ cm}^{-1}$, of the $X00$ ground state derived from a similar level of theory \[28\]. Note that this value is 0.002 cm$^{-1}$ smaller than the correction calculated directly with the four-particle wave function of the $X00$ state \[5\], which will have to be accounted for when we estimate the uncertainties of the present results.
The leading radiative contribution (to the electronic part of the problem)\cite{27,29–31} is

\[
\mathcal{H}^{(5)} = \frac{4}{3} \left[ \frac{19}{30} - 2 \ln \alpha - \ln K \right] \sum_{i=1}^{2} \sum_{a=1}^{2} \delta(r_{ia}) \\
+ \left[ \frac{164}{15} + \frac{14}{3} \ln \alpha \right] \delta(r_{12}) - \frac{7}{6\pi} P(1/r_{12}^3) \tag{3}
\]

which we evaluated with accurate electronic wave functions along a series of nuclear configurations. The \(\ln K\) non-relativistic Bethe-logarithm was also treated within the BO approximation similarly to Ref.\cite{32}. The \(\ln K(R)\) values for the \(EF\) electronic state were approximated with the \(\ln K(R)\) function of the ion core of \(EF\), so we could use the accurate \(\ln K(R)\) values of (the lowest electronic state of) \(H^+_2\) computed by Korobov\cite{23,33}. The one- and two-electron Darwin corrections were obtained similarly to the relativistic correction, \(i.e.,\) by computing the expectation value of the \(R\)-dependent Darwin correction curves with the pre-BO wave function for each \(N\). We computed the Araki–Sucher (AS) correction for the \(EF\) state in the present work using accurate electronic wave functions (obtained within the BO module of QUANTEN using floating ECGs\cite{14,15}) and the integral transformation technique\cite{34}. The AS correction to each \(E0N\) state was obtained as the expectation value of the correction curve with the four-particle wave function. The \(EF\) corrections were found to be an order of magnitude smaller, \(-0.001\ \text{cm}^{-1}\), than the correction for the ground state, \(-0.013\ \text{cm}^{-1}\)\cite{6,31}. By summing up all these contributions, we obtain the leading radiative correction to the energy, which changes from \(0.385\ \text{cm}^{-1}\) to \(0.379\ \text{cm}^{-1}\) as \(N\) increases from 0 to 5, and we used the \(0.736\ \text{cm}^{-1}\) value for the ground state, compiled from Refs.\cite{6,28}, to calculate the \(\delta T_{\text{rad}}\) term corrections listed in Table II.

Higher-order radiative corrections were estimated at the one-loop level by retaining only the dominant terms in the expressions\cite{32,35}

\[
\mathcal{H}^{(6)}_{\text{est}} = \alpha^4 \pi \left( \frac{427}{96} - 2 \ln 2 \right) \sum_{i=1}^{2} \sum_{a=1}^{2} \delta(r_{ia}) \tag{4}
\]

\[
\mathcal{H}^{(7)}_{\text{est}} = -\alpha^5 4 \ln^2(\alpha) \sum_{i=1}^{2} \sum_{a=1}^{2} \delta(r_{ia}). \tag{5}
\]
While the $\mathcal{H}_{\text{rest}}^{(6)}$ contribution to the $E0N-X00$ term values is $-0.003 \text{ cm}^{-1}$, the $\mathcal{H}_{\text{rest}}^{(7)}$ changes the terms by as little as $2 \cdot 10^{-4} \text{ cm}^{-1}$, which is negligible at the current precision.

The overall $\delta T^{(4-7)}$ contribution (Table III) of the relativistic, radiative, and higher-order radiative effects increases from 0.122 to 0.146 cm$^{-1}$ upon the increase of $N = 0$ to 5. The resulting $T^{(2-7)}$ term values for $N = 0, \ldots, 5$ show $\pm 0.001 \text{ cm}^{-1}$ deviations from the experimental values of Ref. [36], which is better (probably fortu-

The experimental values of Ref. [36] are more precise than our theoretical results, and the additional significant digits surely hide interesting physics, so theory should aim for further improvements. In order to help future work, we close this article with commenting on the possible sources of uncertainties in our work.

First of all, the non-relativistic energy was obtained in a variational procedure (stabilized for long-lived resonances), and systematic improvement of this value is rather straightforward. The convergence pattern observed in repeated rounds of refinement cycles suggests that the non-relativistic energy, $E_{\text{nr}}^{(2)}$, is within a few $10^{-9} E_h$ of its exact value (in the worst case), which translates to $< 0.0005 \text{ cm}^{-1}$. Assessment of the uncertainty of the relativistic and radiative corrections is more delicate. In the light of the developments of recent years for the rovibronic ground state [5, 6, 28, 35], we think that the largest source of error in our work must be due to the relativistic ‘recoil’ effect, on the order of a few $10^{-3} \text{ cm}^{-1}$, which in simple terms means that (at least) the relativistic corrections should be computed directly with the four-particle wave functions. Then, in order to pinpoint one-two more digits in the calculations, the current approximations used for the non-relativistic Bethe-logarithm term will have to be checked and the contribution of the neglected terms in the higher-order radiative corrections (in particular, the full $ma^6$ contribution of $\mathcal{H}^{(6)}$) will have to be elaborated.

In the usual perturbative manner, relativistic quantum electrodynamics (and possibly beyond) is adapted for molecular computations, it is necessary to evaluate and sum several, small (and often not so small) contributions (of different signs) on top of a direct, variational non-relativistic computation. We think that the extremely rich
excited state, rovibronic level structure of the hydrogen molecule (Figure 1) offers an excellent opportunity to challenge and cross-check the theoretical and computational procedures both in terms of the completeness of the physical description as well as regarding the error balance of possible uncertainties and inaccuracies.

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FIG. 1: Born–Oppenheimer potential energy curves for singlet gerade states of H$_2$ compiled from Refs. [25, 37–39]. The ground-state curve of H$_2^+$ [40] is also shown. The present work is concerned with rovibronic states which can be assigned to the $EF^1\Sigma^+_g$ electronic state.
TABLE I: Variational, non-relativistic four-particle energy, in $E_h$, corresponding to the $N = 0, 1, \ldots, 5$ rotational states of the ground vibrational state in the inner well, 'E0N', of the $EF (\Sigma_g^+)$ electronic state of $H_2 = \{e^-, e^-, p^+, p^+\}$. The term values, in cm$^{-1}$, are given with respect to the rovibronic ground state. To obtain these singlet ($S_e = 0$) states, the parity and the proton spin were chosen to be $p = (-1)^N$ and $S_p = (1 - p)/2$, respectively. $E^{(2)}_{nr}$ is estimated to be converged within ca. 1 n$E_h$.

| $N$ | $E^{(2)}_{nr}$ | $T^{(2)}_{nr}$ a | $\Delta T^{(2)}_{o-c}$ b | $\Delta T^{(2)}_{o-c}$ c |
|-----|----------------|-----------------|------------------|------------------|
| 0   | -0.712197577   | 99164.664       | 0.123            | 0.320            |
| 1   | -0.711908569   | 99228.094       | 0.124            | 0.321            |
| 2   | -0.711332945   | 99354.429       | 0.128            | 0.304            |
| 3   | -0.710475421   | 99542.633       | 0.133            | 0.312            |
| 4   | -0.709342932   | 99791.186       | 0.138            | 0.32             |
| 5   | -0.707944454   | 100098.116      | 0.145            | 0.33             |

a $T^{(2)}_{nr} = E^{(2)}_{nr} - E^{(2)}_{nr}(X00)$ where the ground-state energy is $E^{(2)}_{nr}(X00) = -1.164025031 E_h$ [6].

b $\Delta T^{(2)}_{o-c} = T_o - T^{(2)}_c$ with the $T_o$ experimental term values taken from Ref. [36] and $T^{(2)}_c = T^{(2)}_{nr}$.

TABLE II: Perturbative relativistic and radiative corrections up to estimates for $m_0 a^7$ (see text), in cm$^{-1}$, to the E0N–X00 term values of $H_2$ reported in Table I. The relativistic and radiative corrections are estimated to be accurate within a few times $10^{-3}$ cm$^{-1}$.

| $N$ | $\delta T^{(4)}_{rel}$ a | $\delta T^{(5)}_{rad}$ b | $\delta T^{(6,7)}_{brad}$ c | $\delta T^{(4,7)} d$ | $T^{(2,7)} e$ | $\Delta T^{(2,7)} f$ |
|-----|-------------------------|--------------------------|--------------------------|-----------------|-------------|----------------|
| 0   | 0.475                   | -0.351                  | -0.0027                  | 0.123           | 99164.786   | 0.001         |
| 1   | 0.478                   | -0.351                  | -0.0027                  | 0.124           | 99228.217   | 0.001         |
| 2   | 0.482                   | -0.352                  | -0.0027                  | 0.127           | 99354.557   | 0.001         |
| 3   | 0.488                   | -0.353                  | -0.0027                  | 0.132           | 99542.764   | 0.000         |
| 4   | 0.496                   | -0.355                  | -0.0027                  | 0.138           | 99791.326   | 0.000         |
| 5   | 0.506                   | -0.357                  | -0.0028                  | 0.146           | 100098.265  | -0.001        |

a Relativistic correction.

b Leading radiative correction.

c $\delta T^{(6,7)} = \delta T^{(6)} + \delta T^{(7)}$ higher-order radiative corrections estimated by the dominant contributions to the one-loop term.

d $\delta T^{(4,7)} = \delta T^{(4)} + \delta T^{(5)} + \delta T^{(6)} + \delta T^{(7)}$.

e $T^{(2,7)} = T^{(2)} + \delta T^{(4,7)}$.

f $\Delta T^{(2,7)}_{o-c} = T_o - T^{(2,7)}$ with the $T_o$ experimental term values taken from Ref. [36].