Vibronic mass computation for the $EF-GK-H\bar{H}$ $^3\Sigma^+_g$ manifold of molecular hydrogen

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A variational procedure is described for the computation of the non-adiabatic mass correction tensor applicable for multi-dimensional electronic manifolds. The 30-year old computations of Wolniewicz, Dressler and their co-workers are appended with the computed vibronic mass functions corresponding to the $EF-GK-H\bar{H}$ $S5-S6$ $^1\Sigma^+_g$ manifold of the hydrogen molecule. Initial results are reported for the vibronic energies including effective vibronic masses. Necessary further improvements and further developments are discussed.

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I. INTRODUCTION

This paper is dedicated to the memory of L. Wolniewicz.

Wolniewicz, Dressler and their co-workers published a series of papers on the theoretical (and experimental) study of the electronic-vibrational-rotational spectroscopy of molecular hydrogen [1–8]. In their work, the rovibronic wave function was expanded in terms of sum of products of electronic and rovibrational basis functions.

This approach can, in principle, converge to the exact non-relativistic result, if a sufficiently large electronic and vibrational basis set is included in the computation. In a practical computation, the basis set always has to be truncated. Yu and Dressler [8] included five coupled $^1\Sigma_g^+$ states (labelled as $EF$, $GK$, $HH$, $S5$, and $S6$) [7] to describe the vibronic ($J = 0$) states. For the rovibronic ($J > 0$) computations, the electronic space was extended with $^1\Pi$ and $^1\Delta$ wave functions.

It has been pointed out, e.g., Refs. [9–11] that the electronic basis truncation error in the approximate (ro)vibronic energies is of order $O(\varepsilon)$ that may be too large for spectroscopic purposes, where $\varepsilon^2 = m_e/m_p$ is the electron-to-proton mass ratio. A better approximation is obtained if the effect of the discarded electronic subspace is perturbatively corrected. The effective rovibronic Hamiltonian that is an order of magnitude better, i.e., $O(\varepsilon^2)$, contains a kinetic or as it is also called ‘mass-correction’ term. The effective Hamiltonian for a multi-dimensional electronic manifold has been recently formulated [11] following Refs. [9, 10].

The mass-correction term appearing in the $O(\varepsilon^2)$ effective Hamiltonian contains the reduced resolvent of the electronic Hamiltonian, for which a direct summation over the electronic basis may return inaccurate results. In the present work, we adopt Schwartz’ method [12], commonly used for the precise evaluation of the sum-over-states expression in the Bethe logarithm, for the computation of the mass-correction matrix. The sum-over-states contribution, is represented by a ‘perturbed’ wave function that can be systematically improved through the minimization of an appropriate functional.

The vibronic mass correction is evaluated for single and multi-dimensional electronic subspaces corresponding to the $EF$, $GK$, $HH$, $S5$, and $S6$ $^1\Sigma_g^+$ electronic manifold of molecular hydrogen. The computed vibrational mass correction functions are used to complement the work of Wolniewicz, Dressler, and their co-workers, and initial results are reported for the vibronic energies corresponding to effective vibronic masses.

II. NUCLEAR-MOTION HAMILTONIAN OVER COUPLED ELECTRONIC STATES

Eigenstates of the $\hat{H}$ (non-relativistic) electron-nucleus Hamiltonian are approximated over an ansatz of products of electronic and vibrational functions. In this work, we assume an adiabatic electronic basis, $\psi_1(R), \ldots, \psi_g(R)$ ($R$ labels the nuclear coordinates), i.e., the electronic basis functions are eigenfunctions of the electronic Hamiltonian,

$$H(R)\psi_\alpha(R) = E_\alpha(R)\psi_\alpha(R),$$

but only a finite, d-dimensional electronic subspace

$$P = \sum_{\alpha=1}^{d} P_\alpha \quad \text{with} \quad P_\alpha = |\psi_\alpha(R)\rangle\langle\psi_\alpha(R)|$$

is retained for the computation, where $\langle\psi_\alpha(R)|\psi_\beta(R)\rangle = \delta_{\alpha,\beta}$. The Hamiltonian for the quantum nuclear motion over the $P$ electronic subspace reads as

$$\langle\hat{H}_P\rangle_{\alpha,\beta} = \langle\psi_\alpha|\hat{H}_P|\psi_\beta\rangle = \langle\psi_\alpha|\hat{K}|\psi_\beta\rangle + \langle\psi_\alpha|H|\psi_\beta\rangle,$$

where the nuclear kinetic energy part is

$$\langle\psi_\alpha|\hat{K}|\psi_\beta\rangle = -\sum_i \left(\frac{1}{2}(\varepsilon\partial_i)^2\delta_{\alpha,\beta} + \varepsilon\langle\psi_\alpha|\partial_i\psi_\beta\rangle(\varepsilon\partial_i) + \frac{\varepsilon^2}{2}\langle\psi_\alpha|\partial_i^2\psi_\beta\rangle\right).$$
If the \( P \) electronic subspace is separated by a finite gap from the rest of the electronic spectrum over the nuclear coordinates relevant for the nuclear dynamics, then qualitatively correct energy estimates can be expected from this truncated, \( d \)-dimensional description, Eq. (2). Eigenvalues of \( \hat{H}_P \) approximate the exact electron-nucleus non-relativistic energies with an error of \( \mathcal{O}(\varepsilon) \) [9, 11].

Better estimates can be obtained if the electronic states which are not included in the \( P \) subspace are accounted for perturbatively.

To obtain an \( \varepsilon \)-order more accurate energies, a \( \hat{H}^{(2)}_P \) second-order effective Hamiltonian operator has been formulated [11] following earlier work [9, 10]. The matrix representation of this effective Hamiltonian for the rovibrational motion, over the \( \psi_\alpha (\alpha = 1, \ldots, d) \) adiabatic basis is

\[
(\hat{H}^{(2)}_P)_{\alpha\beta} = \langle \psi_\alpha | \hat{H}^{(2)}_P | \psi_\beta \rangle = \langle \psi_\alpha | \hat{K} | \psi_\beta \rangle + \langle \psi_\alpha | \hat{H} | \psi_\beta \rangle + \frac{\varepsilon^2}{2} \sum_{j,i} \sum_{a,b} (\varepsilon \partial_j) M_{\alpha\beta,ij} (\varepsilon \partial_i) \tag{5}
\]

where \( \partial_j = \partial/\partial R_j \) labels numerical differentiation with respect to the \( j \)th nuclear coordinate and the ‘so-called’ mass-correction matrix is

\[
M_{\alpha\beta,ij} = \sum_{a,b=1}^{d} \langle \psi_\alpha | P_a (\partial_j P) (R_a + R_b) (\partial_i P_b) | \psi_\beta \rangle , \tag{6}
\]

and \( R_a = (H(R) - E_a(R))^{-1} P^\perp \) is the reduced resolvent with \( P^\perp = 1 - P \). If \( \psi_1, \ldots, \psi_d \) form an adiabatic basis set, then the mass-correction matrix simplifies to

\[
M_{\alpha\beta,ij} = (\partial_j \psi_\alpha) (R_a + R_b) (\partial_i \psi_\beta) = (\partial_j \psi_\alpha) (H(R) - E_\alpha (R))^{-1} P^\perp (\partial_i \psi_\beta) + \langle \partial_j \psi_\alpha | (H(R) - E_\beta (R))^{-1} P^\perp (\partial_i \psi_\beta) \rangle . \tag{7}
\]

If a single \( \psi_\alpha \) electronic state spans the \( P \) active space \((d = 1)\), the expression simplifies to

\[
M_{\alpha\beta,ij} = 2 \langle \partial_j \psi_\alpha | R_a | \partial_i \psi_\alpha \rangle = 2 \langle \partial_j \psi_\alpha | (H - E_\alpha)^{-1} (1 - P_\alpha) | \partial_i \psi_\alpha \rangle . \tag{8}
\]

The single-state mass correction, Eq. (8), has been formulated several times [13–16] and was successfully used in spectroscopic applications [15, 17–22]. We are not aware of any computation with the multi-state expression, Eqs. (6) or (7).

In Sec. III, a variational approach is described for the evaluation of \( M_{\alpha\beta,ij} \). In Sec. V, we compute the vibronic mass corrections for the example of the lowest electronically excited \( ^1\Sigma_g^+ \) electronic manifold of molecular hydrogen, and report initial results for the vibronic energy by including the effective vibronic masses. The paper ends with an outlook to further computational, algorithmic and theoretical work.

### III. EVALUATION OF THE MASS CORRECTION MATRIX USING SCHWARTZ’ METHOD

We adapt Schwartz’ method, originally proposed to compute the sum-over-states expression in the non-relativistic Bethe logarithm [12], for the evaluation of the mass matrix elements. The method is first adopted for the ground electronic state. Then, orthogonality constraints and lower boundedness of the functional is discussed for an electronically excited state. In the last step, the evaluation of the mass correction for a multi-dimensional electronic subspace is explained.
A. Non-adiabatic mass for the ground electronic state

A non-adiabatic mass matrix element for the ground electronic state \((E_0, \psi_0)\) reads as

\[
M_{00,ij} = (\partial_i \psi_0 | (H - E_0)^{-1} P_0^+ | \partial_j \psi_0)
= \sum_{n \neq 0} \frac{\langle \partial_i \psi_0 | \psi_n \rangle \langle \psi_n | \partial_j \psi_0 \rangle}{E_n - E_0},
\]

(9)

where the summation includes also integration. Following Schwartz, we re-write the sum-over-states expression, as

\[
M_{00,ij} = \langle \partial_i \psi_0 | \phi_0^{(0,j)} \rangle,
\]

(10)

where the \(\phi_0^{(0,j)}\) ‘perturbed’ wave function minimizes the functional (henceforth, the 0 and \((0, j)\) sub- and superscripts are suppressed for brevity):

\[
\mathcal{W}[\phi, \lambda] = \langle \phi | (H - E_0) | \phi \rangle - 2 \langle \phi | \partial \psi_0 \rangle - \lambda \langle \phi | P_0 \phi \rangle,
\]

(11)

and \(\lambda\) is a Lagrange multiplier introduced to ensure that \(\phi\) is orthogonal to \(\psi_0\), and \(P_0 = |\psi_0\rangle \langle \psi_0|\). In general, the \((\phi | \psi_0\rangle = 0\) orthogonality constraint is not automatically fulfilled, unless some special symmetry condition applies, and it is necessary to ensure the \(n \neq 0\) condition in the sum-over-states expression, Eq. (9).

We need to find the stationary point (minimum) of \(\mathcal{W}\) with respect to the variation of \(\phi\) and \(\lambda\):

\[
\delta_{\phi, \lambda} \mathcal{W} = 0
\]

(12)

that reads in detail for \(\forall \delta \phi\):

\[
0 = \delta \mathcal{W} = 2 \langle \delta \phi | H - E_0 | \phi \rangle - 2 \langle \delta \phi | \partial \psi_0 \rangle - 2 \lambda \langle \delta \phi | P_0 \phi \rangle,
\]

(13)

while variation for \(\lambda\) recovers the orthogonality condition, \(0 = \frac{\partial \mathcal{W}}{\partial \lambda} = 2 \langle \phi | P_0 | \phi \rangle\). Eq. (13) must hold for any \(\delta \phi\), and thus, it is equivalently written as

\[
(H - E_0)|\phi\rangle = |\partial \psi_0\rangle + \lambda P_0|\phi\rangle.
\]

(14)

To obtain an expression for \(\lambda\), we multiply Eq. (14) from the left by the ground-state electronic wave function, \(\langle \psi_0|\)

\[
\langle \psi_0 | (H - E_0) | \phi \rangle = \langle \psi_0 | \partial \psi_0 \rangle + \lambda \langle \psi_0 | P_0 | \phi \rangle
\]

(15)

and obtain after rearrangement

\[
\lambda = -\frac{\langle \psi_0 | \partial \psi_0 \rangle}{\langle \psi_0 | \phi \rangle}.
\]

(16)

By inserting this expression in Eq. (14), we arrive at the linear equation

\[
(H - E_0)|\phi\rangle = |\partial \psi_0\rangle - |\psi_0\rangle \langle \psi_0 | \partial \psi_0\rangle
\]

\[
\Leftrightarrow (H - E_0)|\phi\rangle = P_0^+ |\partial \psi_0\rangle, \quad P_0^+ = 1 - P_0
\]

(17)

which can be solved to obtain the \(\phi\) perturbed wave function. Then, \(\phi\) is used to compute the mass correction elements according to Eq. (10). Parameterization of the basis functions used to represent \(\phi\) can be optimized by minimization of the following functional (instead of the energy functional):

\[
\mathcal{W} = \langle \phi | H - E_0 | \phi \rangle - 2 \langle \phi | \partial \psi_0 \rangle + 2 \langle \phi | \psi_0 \rangle \langle \psi_0 | \partial \psi_0 \rangle
\]

\[
\Leftrightarrow \mathcal{W} = \langle \phi | H - E_0 | \phi \rangle - 2 \langle \phi | P_0^+ | \partial \psi_0 \rangle.
\]

(18)
It is useful to note, by comparing Eqs. (17) and (18), that
\[ \langle \phi | H - E_0 | \phi \rangle = \langle \phi | P_0^+ | \partial \psi_0 \rangle . \]  
(19)

By inserting this result in Eq. (18), we arrive at
\[ \mathcal{W} = -\langle \phi | P_0^+ | \partial \psi_0 \rangle , \]  
(20)
and this simple expression was used to update the value of $\mathcal{W}$ during the course of the basis refinement procedure.

### B. Mass correction for electronically excited states

$\mathcal{W}$ is bounded from below for the ground electronic state, but this is not generally true for electronically excited states, due to the presence of lower-energy states in the Hamiltonian. For the example of the first excited state, we write out $\mathcal{W}$ using the spectral theorem,

\[ \mathcal{W} = \langle \phi | (H - E_1) | \phi \rangle - 2 \langle \phi | P_1^+ | \partial \psi_1 \rangle \]
\[ = \sum_{n=0, n \neq 1}^\infty (E_n - E_1) \langle \phi | \psi_n \rangle \langle \psi_n | \phi \rangle - 2 \langle \phi | P_1^+ | \partial \psi_1 \rangle \]
\[ = (E_0 - E_1) |\langle \phi | \psi_0 \rangle|^2 + \sum_{n>1}^\infty (E_n - E_1) |\langle \phi | \psi_n \rangle|^2 - 2 \langle \phi | P_1^+ | \partial \psi_1 \rangle \]  
(21)

and similarly, for the $k$th electronic state,

\[ \mathcal{W} = \langle \phi | (H - E_k)^{-1} | \phi \rangle - 2 \langle \phi | P_k^+ | \partial \psi_k \rangle \]
\[ = \sum_{i=0, i \neq k}^{k-1} (E_i - E_k) |\langle \phi | \psi_i \rangle|^2 + \sum_{n>k}^\infty (E_n - E_k) |\langle \phi | \psi_n \rangle|^2 - 2 \langle \phi | P_k^+ | \partial \psi_k \rangle \]  
(22)

is not bounded from below with respect to the variation of $\phi$.

We can proceed as follows. First, we exclude the contribution of the (finite many) lower-energy states, next, adapt Schwartz’ method to compute the contribution from the (infinitely) many higher-energy states, and in the end, we obtain the total mass correction value by adding the contribution of the $k$ lower-energy states by explicit summation.

To implement this idea, we have to write the functional with $k+1$ auxiliary conditions that ensure the orthogonality of the $\phi^<$ perturbed wave function to all lower-energy states as well as to the $k$th eigenfunction (the superscript $<$ is used to remind ourselves that the perturbed wave function now carries information only about the higher-energy states):

\[ \mathcal{W} = \langle \phi^< | (H - E_k) | \phi^< \rangle - 2 \langle \phi^< | \partial \psi_k \rangle \]  
(23)
with the auxiliary orthogonality conditions
\[ \langle \phi^< | P_i | \phi^< \rangle = 0 , \quad i = 0, \ldots, k \]  
(24)
with $P_i = |\psi_i\rangle \langle \psi_i|$ and we imply during this calculation that $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ is fulfilled (the calculation can be generalized to non-perfectly orthogonal electronic states that may occur during numerical computations with different, finite basis sets). We label the excluded space by $\mathcal{P} = \sum_{i=0}^k P_i$, which equals $P$ defined in Sec. II, if the mass correction corresponds to a coupled-state description with all electronic states $i = 0, 1, \ldots, k$. If we describe the $k$th electronic state as an isolated state, then $P = P_k$, whereas $\mathcal{P} = \sum_{i=0}^k P_i$, and the contribution of the $0, 1, 2, \ldots, k-1$ states must be computed by explicit summation. Further details regarding a coupled-state description including a few electronically excited states are explained in Sec. III C.
We implement the auxiliary conditions, Eqs. (24), using the method of Lagrange multipliers,

\[ W^{(k)}[\phi, \lambda_0, \ldots, \lambda_k] = \langle \phi^\perp | (H - E_k) | \phi^\perp \rangle - 2 \langle \phi^\perp | \partial \psi_k \rangle - \sum_{i=0}^{k} \lambda_i \langle \phi^\perp | P_i | \phi^\perp \rangle . \]  

Minimization of \( W^{(k)} \) with respect to the variation of \( \phi \) and the \( \lambda_i \)'s assumes the fulfillment of the auxiliary orthogonality conditions, Eqs. (24), and

\[ 0 = 2 \langle \delta \phi^\perp | (H - E_k) | \phi^\perp \rangle - 2 \langle \delta \phi^\perp | \partial \psi_k \rangle - 2 \sum_{i=0}^{k} \lambda_i \langle \delta \phi^\perp | P_i | \phi^\perp \rangle , \quad \forall \delta \phi^\perp \]  

that is equivalent with

\[ (H - E_k) | \phi^\perp \rangle = | \partial \psi_k \rangle + \sum_{i=0}^{k} \lambda_i P_i | \phi^\perp \rangle . \]  

Similarly to Sec. III A, we obtain \( \lambda_j \) by multiplying Eq. (32) from the left by the \( j \)th electronic eigenfunction, \( \langle \psi_j \rangle \):

\[ \langle \psi_j | (H - E_k) | \phi^\perp \rangle = \langle \psi_j | \partial \psi_k \rangle + \sum_{i=0}^{k} \lambda_i \langle \psi_j | \psi_i \rangle \langle \psi_i | \phi^\perp \rangle . \]  

Due to \( \langle \psi_i | \psi_j \rangle = \delta_{ij} \), the expression simplifies to

\[ \langle \psi_j | (H - E_k) | \phi^\perp \rangle = \langle \psi_j | \partial \psi_k \rangle + \lambda_j \langle \psi_j | \phi^\perp \rangle \]  

and we obtain

\[ \lambda_j = \frac{\langle \psi_j | (H - E_k) | \phi^\perp \rangle - \langle \psi_j | \partial \psi_k \rangle}{\langle \psi_j | \phi^\perp \rangle} , \quad j = 0, 1, \ldots, k . \]  

As a result,

\[ (H - E_k) | \phi^\perp \rangle = | \partial \psi_k \rangle + \sum_{i=0}^{k} \frac{\langle \psi_i | (H - E_k) | \phi^\perp \rangle - \langle \psi_i | \partial \psi_k \rangle | \psi_i \rangle \langle \psi_i | \phi^\perp \rangle}{\langle \psi_i | \phi^\perp \rangle} = | \partial \psi_k \rangle + \sum_{i=0}^{k} | \psi_i \rangle \left[ (H - E_k) | \phi^\perp \rangle - \langle \psi_i | \partial \psi_k \rangle \right] = | \partial \psi_k \rangle + \mathcal{P}(H - E_k) | \phi^\perp \rangle - \mathcal{P}_\perp | \partial \psi_k \rangle \]  

that is rearranged to the linear equation

\[ \mathcal{P}_\perp (H - E_k) | \phi^\perp \rangle = \mathcal{P}_\perp | \partial \psi_k \rangle \]  

which is solved to obtain the \( | \phi^\perp \rangle \) perturbed wave function (including the effect of all states with an energy higher than \( E_k \)). Using Eqs. (25) and (30),

\[ W^{(k)}(\phi^\perp) = \langle \phi^\perp | (H - E_k) | \phi^\perp \rangle - 2 \langle \phi^\perp | \partial \psi_k \rangle - 2 \sum_{i=0}^{k} \langle \phi^\perp | (H - E_k) | \phi^\perp \rangle - \langle \psi_i | \partial \psi_k \rangle \langle \phi^\perp | P_i | \phi^\perp \rangle \]

\[ = \langle \phi^\perp | (H - E_k) | \phi^\perp \rangle - 2 \langle \phi^\perp | \partial \psi_k \rangle - 2 \sum_{i=0}^{k} \langle \phi^\perp | \psi_i \rangle \left[ (H - E_k) | \phi^\perp \rangle - \langle \psi_i | \partial \psi_k \rangle \right] \]  

(33)
or in short

\[ W_{A,s}^{(k)} = \langle \phi^\perp | (H - E_s) \mathcal{P}^\perp | \phi^\perp \rangle - 2 \langle \phi^\perp | \mathcal{P}^\perp \partial \psi_k \rangle \]  \hspace{1cm} (34)

is the (non-linear) functional that can be minimized to optimize the basis function parameterization (that we label with \( A \) and \( s \)) to systematically improve the perturbed wave function, \( | \phi^\perp \rangle \). Similarly to Sec. III A, fast evaluation of \( W_{A,s}^{(k)} \) was carried out by computing

\[ W_{A,s}^{(k)} = - \langle \phi^\perp | \mathcal{P}^\perp \partial \psi_k \rangle \]  \hspace{1cm} (35)
during the course of the non-linear optimization.

The mass correction for the \( \alpha \)th isolated, electronically excited state, Eq. (8), is obtained as

\[
M_{\alpha,ij}/2 = \langle \partial_j \psi_\alpha | (H_{el} - E_\alpha)^{-1} \mathcal{P}^\perp | \partial_i \psi_\alpha \rangle \\
= \langle \partial_j \psi_\alpha | \mathcal{P}^\perp | \phi^{(\alpha,i)} \rangle + \sum_{k=0}^\alpha \langle \partial_j \psi_\alpha | \psi_k \rangle \langle \psi_k | \partial_i \psi_\alpha \rangle \frac{E_k - E_\alpha}{E_k - E_\alpha} \\
= \langle \phi^{(\alpha,i)} | \mathcal{P}^\perp | \partial_i \psi_\alpha \rangle + \sum_{k=0}^\alpha \langle \partial_j \psi_\alpha | \psi_k \rangle \langle \psi_k | \partial_i \psi_\alpha \rangle \frac{E_k - E_\alpha}{E_k - E_\alpha},
\]  \hspace{1cm} (36)

where \( \phi^{(\alpha,i)} \) and \( \phi^{(\alpha,j)} \) correspond to the \( \phi \) perturbed wave function computed with \( \partial = \partial_i \) and \( \partial = \partial_j \), respectively. In relation with Eq. (36), it is important to emphasize that \( P_\alpha = |\psi_\alpha \rangle \langle \psi_\alpha| \), whereas \( \mathcal{P} = \sum_{k=0}^\alpha P_k \).

C. Mass correction for coupled electronic manifolds

The ideas outlined for the excited state computation can be straightforwardly used and implemented for a coupled electronic subspace,

\[ P_C = \sum_{n=k_C}^{k_C} |\psi_n \rangle \langle \psi_n| \]  \hspace{1cm} (37)

\( C \) labels the set of the indices of the electronic states that are included in \( P_C \). We will assume that the electronic states are numbered in an increasing energy order, i.e., \( \psi_{k_C} \) is the highest-energy state in the coupled subspace. The general form of the mass-correction coupling between the \( \alpha \)th and \( \beta \)th states from \( P_C \), Eq. (6) (we work in an adiabatic basis), is

\[
M_{\alpha,\beta,ij} = \langle \partial_j \psi_\alpha | \left[ (H - E_\alpha)^{-1} + (H - E_\beta)^{-1} \right] \mathcal{P}_C^\perp | \partial_i \psi_\beta \rangle \\
= \sum_{n \not\in C} \frac{\langle \partial_j \psi_\alpha | \psi_n \rangle \langle \psi_n | \partial_i \psi_\beta \rangle}{E_n - E_\alpha} + \sum_{n \in C} \frac{\langle \partial_j \psi_\alpha | \psi_n \rangle \langle \psi_n | \partial_i \psi_\beta \rangle}{E_n - E_\beta}.
\]  \hspace{1cm} (38)

If \( \alpha \neq \beta \), two perturbed wave functions are computed. For example,

\[ \langle \phi^{(j,\alpha)}_\alpha \rangle = \sum_{n > k_C} \frac{\langle \partial_j \psi_\alpha | \psi_n \rangle \langle \psi_n | \psi_\alpha \rangle}{E_n - E_\alpha} \]  \hspace{1cm} (39)

and

\[ | \phi^{(i,\beta)}_\beta \rangle = \sum_{n > k_C} \frac{|\psi_n \rangle \langle \psi_n | \partial_i \psi_\beta \rangle}{E_n - E_\beta}, \]  \hspace{1cm} (40)

where the infinite sums are not computed explicitly, but the perturbed wave functions (left hand side of the equations) are obtained by using the generalized Schwartz’ method (Secs. III A and
Then, the coupled-state mass matrix element is obtained as

\[
M_{\alpha;\beta;j} = \sum_{n=0}^{k_C} \frac{\langle \partial_j \psi_\alpha | \psi_n \rangle \langle \psi_n | \partial_\beta \psi_\beta \rangle}{E_n - E_\alpha} + (\phi^{(j,\alpha)}_C | \partial_j \psi_\beta \rangle + \phi^{(j,\beta)}_C | \partial_\beta \psi_\alpha \rangle).
\]

(41)

IV. IMPLEMENTATION AND COMPUTATIONAL DETAILS

The theoretical approach outlined in Sec. III has been implemented in the in-house developed computer program named QUANTEN (QUANTum mechanical description of Electrons and atomic Nuclei). QUANTEN has recent applications including non-relativistic energy upper and lower bounds, non-adiabatic, pre-Born–Oppenheimer, perturbative and variational relativistic computations [21–32]. The program contains a (stochastic and deterministic) non-linear variational engine and an integral library for variants of explicitly correlated Gaussian (ECG) functions. The electronic wave function is written as a linear combination of anti-symmetrized products of spatial and spin functions. In this work, the spatial functions are floating ECGs,

\[
\varphi(r, A, s) = \exp\left[-(r - s)^T (A \otimes I_3)(r - s)\right],
\]

where \( r \in \mathbb{R}^6 \) collects the Cartesian coordinates of the two electrons, \( A \in \mathbb{R}^{2 \times 2} \) is a symmetric, positive-definite parameter matrix, and the \( s \in \mathbb{R}^6 \) shift vectors are fixed to the proton-proton axis. The functions are adapted to have gerade (g) symmetry, and as a result of this construct, the spatial basis functions have \( \Sigma_g^+ \) symmetry.

The \( X, EF, GK, H\bar{H}, S5, \) and \( S6 \) electronic states are computed with this setup using 1200 ECG functions optimized separately for each electronic state state. First, the electronic energy is converged at a single point (1.4 bohr for the \( X \) state and 3 bohr for the \( EF, \) \( GK, \) and \( H\bar{H} \) states) within a few nEh precision. Then, a series of points is generated by rescaling the centers (s vectors) upon changing the distance (by \( \Delta R = 0.1 \) bohr at every step) using the rescaling procedure proposed by Cencek and Kutzelnigg [33]. After rescaling, we have performed repeated refinement cycles at every new geometry. At a few selected points, the \( S5 \) and \( S6 \) states were computed by running repeated energy refinement cycles for the minimization of the \( S5 \) and \( S6 \) energy starting from the basis optimized for the \( H\bar{H} \) state at the same geometry. The resulting \( S5 \) and \( S6 \) energies are converged within 50-100 nEh, and this value can be reduced to 10 nEh in the present setup without major computational effort.

The wave function derivatives, \( \partial \psi_i \) with respect to the nuclear coordinates have been computed by finite differences and the rescaling procedure of Ref. [33]. Instead of the six Cartesian coordinates of the two protons, we fix the protons center of mass at the origin and use spherical polar coordinates \( (R, \vartheta, \phi) \) to describe the shape and orientation of the molecule. Hence, for the vibronic mass computations, we had to compute only the \( \partial / \partial R \), henceforth \( \partial \), derivative of the electronic states. The \( \partial \psi_i \) function, as well as the \( \phi \) perturbed wave function (Sec. III) have \( \Sigma_g^+ \) symmetry. For this reason, the basis set optimized for the electronic state was usually an excellent starting basis for the \( \phi \) perturbed wave function, and a few refinement steps were performed.

In this initial report, the vibronic mass-correction values have been computed for 26 nuclear configurations (see Supplementary Material). The non-adiabatic coupling and the diagonal and off-diagonal Born–Oppenheimer corrections, Eqs. (3)–(4), are taken from the work of Wolniewicz and Dressler [7], although the Born–Oppenheimer (BO) potential energies are replaced with the PECs computed in the present work. We also note that BO potential energy curves have been recently reported in the literature with a \( 10^{-10} \) relative precision [34] that will be very useful when all other contributions (non-adiabatic, relativistic, and QED) will have been checked and refined.

It was necessary to check the phase of the wave functions \( \langle \partial \psi_i \rangle \) in the bra and in the ket for the off-diagonal elements of the mass-correction tensor. All phases were adjusted with respect to the phases at \( R = 3 \) bohr, and they were adjusted to be identical with the phase corresponding to the non-adiabatic coupling matrix elements taken from Ref. [7] that was checked at single points.

The physical constants and conversion factors used in the computations were taken from the CO-
V. VIBRONIC COMPUTATIONS FOR THE HYDROGEN MOLECULE

A. Vibronic masses

Figures 1 and 2 show the vibronic mass correction values (corresponding to the \( R \) degree of freedom \cite{25}) computed in the present work for the \( EF, GK, \) and \( HH \) electronic states corresponding to a single state description (1-dimensional electronic subspace), and for the \( EF-GK \) (2), the \( EF-GK-HH \) (3), and the \( EF-GK-HH-S5-S6 \) (5) multi-dimensional descriptions. The off-diagonal vibronic mass correction values and all numerical data (points) used to prepare the figures are deposited in the Supplementary Material. Comparison of the computed vibronic energies and experiment is shown in Fig. 3. During the discussion of the results, it may be relevant to inspect also Fig. 4 that provides an overview of the relevant electronic states.

The vibronic mass correction is always positive for the ground state (diagonal elements), but it can also be negative for excited states. We see large negative features in the isolated \( GH \) state due to the nearby, lower-energy \( EF \) state, and it is interesting to note the corresponding (positive) feature in the isolated \( EF \) vibronic mass correction curve. Nevertheless, these features appear to be of purely theoretical interest, since the single-state description of the \( EF \) or the \( GK \) state does not give good results (of spectroscopic quality). For these single-state computations, the second-order perturbative correction is insufficient for an accurate description. Regarding higher-order corrections, already the third-order corrections \cite{11} appear to be numerically very complicated.

In contrast to the \( EF \) and the \( GK \) states, for the outer well of the \( HH \) state (Fig. 4), the single-state adiabatic description was known to give reasonable results and was found to be useful in terms of the assignment of the spectrum \cite{35}. Over this potential energy well, we observe a shallow (negative) minimum of the vibronic mass correction (\( m(1)_{\text{HH}} \) in Fig. 1), \( i.e. \), the effective vibronic mass is smaller than the mass of the proton. This feature was computed already in Ref. \cite{21}, and it was found that correction of the constant, nuclear (proton) mass by this non-adiabatic term the deviation of theory and experiment is reduced by an order of magnitude, \( i.e. \), from ca. 1 cm\(^{-1} \) to ca. 0.1 cm\(^{-1} \). (We note that in both the single-state adiabatic and non-adiabatic computations relativistic and leading-order QED corrections were included in Ref. \cite{21}.)

For further improvement, it would be necessary either to account for higher-order perturbative corrections, which is numerically very complicated, or to replace the 1-dimensional electronic subspace with a multi-dimensional subspace by including the nearby-lying electronic states in the coupled electronic subspace that is feasible and subject of the present work.

VI. VIBRONIC ENERGIES

Following Wolniewicz, Dressler and their co-workers \cite{1, 2, 5, 7, 8} the non-adiabatic wave function is expanded as

\[
\Psi = \sum_{\alpha \in C} \psi_{\alpha}(r) \frac{1}{R} f_{\alpha}(R) = \frac{1}{R} \psi f ,
\]

and the vibrational part of the wave function satisfies

\[
\left\{ -\frac{1}{2\mu} \left[ \frac{d}{dR} \left( I - \frac{1}{2\mu} m \right) \frac{d}{dR} + A + B \frac{d}{dR} \right] + U \right\} f = Ef ,
\]

where \( \mu = m_p/2 \) is the reduced mass, \( I_{\alpha\beta} = \delta_{\alpha\beta} \), and the \( A_{\alpha\beta} \) and \( B_{\alpha} \) coupling functions were taken from Ref. \cite{7}. We use the adiabatic representation, hence \( (U)_{\alpha\beta} = \delta_{\alpha\beta} V_{\alpha} \) is diagonal. The vibronic mass correction elements, \( m_{\alpha\beta} \), and the BO PECs, \( V_{\alpha} \), were computed in the present work. Simple truncation of the electronic space, Eqs. (3)–(4), corresponds to neglecting \( m \) in Eq. (44), whereas solving the complete Eq. (44) corresponds to the second-order effective Hamiltonian, Eq. (5).

\[
\text{DATA18 recommendation, } m_{\alpha}/m_e = 1.836.152.673.43(11) \text{ and } 1 \ E_h = 219.474.631.363.20(43) \text{ cm}^{-1} .
\]
Figure 1. Overview of the diagonal vibronic mass correction values for the EF, GK, and \( \bar{HH} \) electronic states corresponding to a one- (1: \( EF / GK / \bar{HH} \)), two- (2: \( EF - GK \)), three- (3: \( EF - GK - \bar{HH} \)), and five-dimensional (5: \( EF - GK - \bar{HH} - S5 - S6 \)) coupled electronic manifold. Small features can be better observed in the \( n \)-fold enlargement (\( \times n \)) of the functions plotted in dashed line.
shows the deviation of the experimental order QED corrections, is in progress. The computation of the non-relativistic Bethe logarithm, which appears in the leading-term value, the computed term values overestimate the experimental values, whereas when the mass corrections are included the computed non-relativistic term value is typ-

Figure 2. Diagonal vibronic mass correction values for the S5 and S6 electronic states described within the five-dimensional coupled electronic manifold.

Table I. Comparison of the four-particle, pre-Born–Oppenheimer (preBO) [28] and non-adiabatic (nad) energies (this work) for the lowest vibrational level corresponding to the $EF\ ^1\Sigma_u^+$ electronic state.

| Coupled states | Mass $^*$ | $T_{\text{preBO}} - T_{\text{nad}}$ [cm$^{-1}$] |
|----------------|----------|---------------------------------|
| $EF$–$GK$–$HH$ | $m_p$ | $-0.28$ |
| $EF$–$GK$–$HH$ | $m_{\text{eff}}$ | $0.14$ |
| $EF$–$GK$–$HH$–$S5$–$S6$ | $m_p$ | $-0.27$ |
| $EF$–$GK$–$HH$–$S5$–$S6$ | $m_{\text{eff}}$ | $-0.05$ |

$^*$: $m_p$ and $m_{\text{eff}}$ refer to Eq. (44) without and with the $\bf{m}$ vibronic mass correction term, respectively.

We note that $\bf{m}$ corresponds to the matrix representation over the $\psi_\alpha \in P_C$ electronic eigenfunctions (adiabatic representation) of the $R, R$ element of the mass-correction tensor, Eq. (7), expressed in spherical polar coordinates [25].

To solve Eq. (44), we used the associated Laguerre polynomials, $L_n^{(\alpha)}$ with $\alpha = 2$ and the discrete variable representation (DVR) [36] for every $f_\alpha(R)$ function similarly to Refs. [25, 26].

Although the present computations do not contain relativistic and QED corrections, comparison of the vibronic term values with experiment is relevant, because we think that non-adiabatic effects have an important role in the earlier deviation of theory and experiment [8], which is larger than 1 cm$^{-1}$ for several states. For this comparison, we have calculated the non-relativistic term value, $T = E - E_{\text{X0,nn}}$, where $E_{\text{X0,nn}}$ is the non-relativistic, non-adiabatic energy of the rovibronic ground state (X0). We use $E_{\text{X0,nn}} = -1.164\ 625\ 631$ E$_h$ [15] that is sufficiently precise for this work, but we note that further digits are available [37]. Regarding the experimental values, we use the dataset from Ref. [38], but we also note that for some of the terms corresponding to the $EF$ [39], the $GK$ and the $HH$ (inner well) states [40] more precise experimental data has become available since Ref. [38] that is beyond the current theoretical accuracy.

Direct comparison of the computed non-adiabatic energies would be most appropriate with pre-Born–Oppenheimer (preBO, here: four-particle) energies, which do not contain relativistic and QED effects. In the $^1\Sigma_u^+$ manifold, the preBO energy is available only for the vibrational ground state ($E\ 0$ and its rotational excitations) corresponding to the $EF$ electronic state [28]. For the $E\ 0$ state the comparison is shown in Table 1.

Figure 3 shows the deviation of the experimental [38] and non-relativistic, non-adiabatic term values corresponding to coupling 2 ($EF$–$GK$), 3 ($EF$–$GK$–$HH$), and 5 ($EF$–$GK$–$HH$–$S5$–$S6$) electronic states. Before inclusion of the relativistic and QED corrections, which would allow direct comparison of theory and experiment, further improvements to the current computations will be necessary. The computation of the non-relativistic Bethe logarithm, which appears in the leading-order QED corrections, is in progress [41]. At the present stage, we may observe that without the non-adiabatic mass corrections, the computed term values overestimate the experimental values,
ically larger in this range than the experimental term energy. The preBO study of the $EF$ levels [28] shows that the relativistic and QED corrections to the term value is negative, which suggests that the current inclusion of the non-adiabatic masses does improve upon the truncated (proton mass) results (see also Table 1).

For higher-energy states, we observe that inclusion of the effective vibronic masses can shift the term values by several (tens of) wave numbers to lower energies, which correspond to a positive shift in the energy levels by values as large as 5–20 cm$^{-1}$. It is necessary to note that a large shift can indicate that (a) second-order perturbation theory is insufficient (and we would need to include higher-order terms); or (b) the actively coupled electronic space is too small, or in other words, the energy gap between the coupled space and the discarded states is too small.

The third-order terms [11] appear to be too complicated (at the moment) for numerical evaluation, while, enlargement of the coupled space is feasible, although it raises some further (fundamental) questions for the theory (see Sec. VII and Fig. 4).

How can we improve upon the current results results?

There is ample space for improvements. First of all, it will be necessary to recompute the coupling functions, $A$ and $B$ in Eq. (44), more precisely, and to compute the non-adiabatic mass corrections at more points along the PECs. It also appears to be necessary to add a few more electronic states to the actively coupled manifold that should also be computationally feasible.

It is necessary to note however that if a higher-energy actively coupled electronic state is close to another electronic state not included in $P_{C}$, then it can have a large mass-correction value (that may cause computational instabilities), while its contribution to the dynamics in the interesting energy range may be small. We have experienced this problem for the $m^{(3)}_{H}$ value in the $EF$–$GK$–$HH$ computation, and we handled it with an ad hoc numerical damping. So, in practice, instead of 2680, we used 500 at the maximum of the $m^{(3)}_{H}$ peak near $R = 3$ bohr (Fig. 1). This makes the numerical computations more stable, but it introduces some uncertainty (ca. 0.02–0.1 cm$^{-1}$) in the higher energy range.

So, the question arises: how many more electronically excited states do we need to couple to have precise energies for the $EF$–$GK$–$HH$ manifold? Is the gap condition of perturbation theory [9] well fulfilled in practice, i.e., is it possible to choose the subspace so that there is a sufficiently large gap of the coupled states and the rest? In other words, is the second-order effective Hamiltonian, Eq. (5), sufficient to obtain accurate rovibronic energies? Regarding higher excited PECs of $H_{2}$ (from the $^{1}Sigma_g^{+}$ manifold), Corongiu and Clementi computed many states, including many $^{1}Sigma_g^{+}$ states, of the $H_{2}$ molecule with a ca. $10^{-5} E_{0}$ precision [42, 43]. Excited $nSigma_g^{+}$ states up to $n = 7$ have been computed with a relative precision of $10^{-16}$ (0.000 02 cm$^{-1}$) by Siłkowski, Zientkiewicz, and Pachucki [34]. Figure 4 shows the PECs used in this work and the electronic energy of the $nSigma_g^{+}$ states at $R = 3$ bohr proton-proton distance up to the BO energy of the $^{2}Sigma_g^{+}$ state of $H_{2}$. At $R = 3$ bohr, we have found 17 electronic states below the $^{2}Sigma_g^{+}$ energy value, which indicates that in this region, i.e., beyond 124 000 cm$^{-1}$ up to ionization, there is a very high density of states, ca. 556 cm$^{-1}$ per state.

VII. SUMMARY, CONCLUSION, AND OUTLOOK

A variational approach has been reported for the computation of the non-adiabatic mass correction matrix that includes a sum-over-states expression. The approach can be used for isolated ground or electronically excited states, as well as for coupled electronic subspaces.

Initial results have been reported about of the vibronic mass correction for the $EF$–$GK$–$HH$–$S5$–$S6$–$^{1}Sigma_g^{+}$ manifold and the effect of the mass correction term on the vibronic energies. For a direct comparison with experiment, it is necessary to account for the relativistic and leading-order QED corrections, for which the computation of the Bethe logarithm is in progress [41].

In future work, it will be necessary to (a) compute more precise coupling matrix elements, (b) compute the mass correction values at more points, and (c) possibly couple more electronic states. At the same time, the high density of electronic states beyond the $HH$ state (Fig. 4) may require further development of the theory.
Figure 3. Deviation of the experimental \[38\] and computed term values corresponding to the electronically excited \(1\Sigma^+_g\) manifold of molecular hydrogen. \(T_{\text{comp}} = E - E_{X0,nr}\) with the \(E_{X0,\text{nr}} = -1.164 025 031\ \text{E}_\text{h}\) \[15\] non-relativistic energy of the vibronic ground state (X0). The computed \(E\) energies are obtained from explicit coupling of 2 (\(\text{EF–GK}\)), 3 (\(\text{EF–GK–HH}\)), and 5 (\(\text{EF–GK–HH–S5–S6}\)) electronic states using the nuclear mass \(m_p\) or including also the vibronic mass correction \(m_{\text{eff}}\) that corresponds to solving Eq. (44) without or with the \(m\) correction term, respectively. In the \(\text{EF–GK}\) subfigure no datapoints are shown beyond the fundamental HH vibrational energy.
Figure 4. The $E_F$, $GK$, $HH$, $S5$, and $S6$ $^1\Sigma^+_g$ BO potential energy curves considered in this work. The red points highlight the $n$ $^1\Sigma^+_g$ with $n = 1, \ldots, 17$ potential energy values that we computed below the $^2\Sigma^+_g$ ground-state energy of $H_2^+$ at $R = 3$ bohr internuclear separation. The potential energy curve of $H_2^+$ was taken from Ref. [44].

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