Supplementary Material

High-Precision Quantum Dynamics of He_2 over the b $^3\Pi_g$-c $^3\Sigma_g^+$ Electronic Subpsace by including Non-adiabatic, Relativistic and QED Corrections and Couplings

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CONTENTS

The numerical values of the physical constants and conversion factors were taken from CODATA 2022 [1]; they are $\alpha = 0.007\ 297\ 352\ 564\ 3$, $1\ E_\mathrm{h} = 219\ 474.631\ 363\ 14\,(hc)\mathrm{cm}^{-1}$, and the mass of the helium nucleus, $M(^4\mathrm{He}) = 7\ 294.299\ 541\ 71\ m_\mathrm{e}$, $E_\mathrm{h} = 6.5796839204999 \cdot 10^{+9}\ (h\,\mathrm{MHz})$.

S1. LEADING-ORDER RELATIVISTIC AND QED CORRECTION TERMS

In this section, we provide a short summary of the expressions used; further implementation details are reported for the spin-independent terms in Refs. 2, 3 and for the spin-dependent terms in Ref. 4. The electronic energy is approximated as the sum of the non-relativistic energy, $E_\mathrm{x}^{(0)}$ (with wave function, $\varphi_\mathrm{x}^{(0)}$; solutions of electronic Schrödinger equation), and relativistic and quantum electrodynamics (QED) corrections written as powers of the α fine-structure constant,

$$E_\mathrm{x} = E_\mathrm{x}^{(0)} + \alpha^2\langle\varphi_\mathrm{x}^{(0)}|\hat{H}^{(2)}_\mathrm{BP,sn}|\varphi_\mathrm{x}^{(0)}\rangle + \alpha^2\langle\varphi_\mathrm{x}^{(0)}|\hat{H}^{(2)}_\mathrm{BP,sd}|\varphi_\mathrm{x}^{(0)}\rangle + \alpha^3 E_\mathrm{x}^{(3)} + \alpha^3\langle\varphi_\mathrm{x}^{(0)}|\hat{H}^{(3)}_\mathrm{sd}|\varphi_\mathrm{x}^{(0)}\rangle \tag{S1}$$

For convenience, we write the relativistic and QED corrections as the sum of the spin-independent (sn) centroid correction and spin-dependent (sd) terms. The electronic states considered in this work have different spatial symmetries; therefore, we do not require any off-diagonal centroid corrections. However, the spin-dependent terms introduce off-diagonal electronic contributions, which we compute and utilise for predicting the fine-structure splitting of the rovibronic states. In this work, the electronic states with 'x': b, c, B, and C are considered.

The spin-independent relativistic correction is obtained as the expectation value with the non-relativistic wave function for the Breit-Pauli (BP) Hamiltonian,

$$\hat{H}^{(2)}_\mathrm{BP,sn} = \hat{H}_\mathrm{MV} + \hat{H}_\mathrm{D1} + \hat{H}_\mathrm{OO} + \hat{H}_\mathrm{D2} + \hat{H}_\mathrm{SS,c} \tag{S2}$$

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with the mass-velocity, the one-electron Darwin, the two-electron Darwin and the orbit-orbit terms, and the Fermi contact part of of the spin-spin interaction

$$\hat{H}_{\rm MV} = -\frac{1}{8}\sum_{i=1}^{n_{\rm e}} (\hat{\boldsymbol{p}}_i^2)^2 \;, \tag{S3}$$

$$\hat{H}_{\rm D1} = \frac{\pi}{2}\hat{\delta}_1 \quad , \quad \hat{\delta}_1 = \sum_{i=1}^{n_{\rm e}}\sum_{A=1}^{N_{\rm nuc}} Z_A \delta(\boldsymbol{r}_{iA}) \;, \tag{S4}$$

$$\hat{H}_{\rm OO} = -\frac{1}{2}\sum_{i=1}^{n_{\rm e}}\sum_{j=i+1}^{n_{\rm e}} \left[\frac{1}{r_{ij}}\hat{\boldsymbol{p}}_i\hat{\boldsymbol{p}}_j + \frac{1}{r_{ij}^3}(\boldsymbol{r}_{ij}(\boldsymbol{r}_{ij}\hat{\boldsymbol{p}}_j)\hat{\boldsymbol{p}}_i)\right] \;, \tag{S5}$$

$$\hat{H}_{\rm D2} = -\pi\hat{\delta}_2 \quad , \quad \hat{\delta}_2 = \sum_{i=1}^{n_{\rm e}}\sum_{j=i+1}^{n_{\rm e}} \delta(\boldsymbol{r}_{ij}) \;, \tag{S6}$$

$$\hat{H}_{\rm SS,c} = -\frac{8\pi}{3}\sum_{i=1}^{n_{\rm e}}\sum_{j=i+1}^{n_{\rm e}} \hat{\boldsymbol{s}}_i\hat{\boldsymbol{s}}_j\delta(\boldsymbol{r}_{ij}) \;, \tag{S7}$$

respectively, and $\hat{\boldsymbol{s}}_i = I(1)\otimes ... \otimes \frac{1}{2}\boldsymbol{\sigma}(i) \otimes ... \otimes I(n_{\rm e})$.

The leading-order QED correction to the centroid energy is

$$\begin{aligned} E_{\rm x}^{(3)} = {} & \frac{4}{3}\left[\frac{19}{30} - 2\ln\alpha - \ln(k_0)_{\rm x}\right]\langle\varphi_{\rm x}^{(0)}|\sum_{i=1}^{n_{\rm e}}\sum_{A=1}^{N_{\rm nuc}} Z_A\delta(\boldsymbol{r}_{iA})|\varphi_{\rm x}^{(0)}\rangle \\ & + \left[\frac{164}{15} + \frac{14}{3}\ln\alpha\right]\langle\varphi_{\rm x}^{(0)}|\sum_{i=1}^{n_{\rm e}}\sum_{j=i+1}^{n_{\rm e}}\delta(\boldsymbol{r}_{ij})|\varphi_{\rm x}^{(0)}\rangle - \frac{7}{6\pi}\langle\varphi_{\rm x}^{(0)}|\sum_{i=1}^{n_{\rm e}}\sum_{j=i+1}^{n_{\rm e}}\mathcal{P}\left(1/r_{ij}^3\right)|\varphi_{\rm x}^{(0)}\rangle \;. \end{aligned} \tag{S8}$$

with the Bethe logarithm,

$$\ln(k_0)_{\rm x} = \frac{\left\langle\varphi_{\rm x}^{(0)}|\hat{\boldsymbol{P}}_{\rm e}(\hat{H}_{\rm e} - E_{\rm x})\ln[2|\hat{H}_{\rm e} - E_{\rm x}|]\hat{\boldsymbol{P}}_{\rm e}|\varphi_{\rm x}^{(0)}\right\rangle}{2\pi\langle\varphi_{\rm x}^{(0)}|\hat{\delta}_1|\varphi_{\rm x}^{(0)}\rangle} \;, \tag{S9}$$

where $\hat{H}_{\rm e}$ and $E_{\rm x}^{(0)}, \varphi_{\rm x}^{(0)}$ are the non-relativistic Hamiltonian and the electronic energy and wave function. $\hat{\boldsymbol{P}}_{\rm e} = \sum_{i=1}^{n_{\rm el}}\hat{\boldsymbol{p}}_i$ is the total momentum of electrons. The Araki-Sucher distribution (with the Euler-Mascheroni constant, γ) is

$$\mathcal{P}\left(\frac{1}{r_{ij}^3}\right) = \lim_{\epsilon\to 0^+}\left[\frac{\Theta(r_{ij}-\epsilon)}{r_{ij}^3} + 4\pi[\gamma + \ln(\epsilon)]\delta(\boldsymbol{r}_{ij})\right] \;. \tag{S10}$$

The Bethe logarithm is approximated by the (single-electron) ion-core value [5, 6] for all electronic states considered in this work (see also Ref. [7]). The AS term is computed for the c state with the integral transform technique [8] over the $\rho \in [1, 10]$ bohr internuclear distances interval, and it is used (as an approximation) for the b, B, and C states. The higher-order QED corrections and finite-nuclear-size effects are neglected in this work.

The leading-order relativistic spin-dependent corrections in the Breit-Pauli Hamiltonian are

$$\hat{H}_{\rm BP,sd}^{(2)} = \hat{H}_{\rm SO} + \hat{H}_{\rm SOO} + \hat{H}_{\rm SOO'} + \hat{H}_{\rm SS,dp} \tag{S11}$$

with the one-electron spin-orbit, the spin-own-orbit, the spin-other-orbit, and the magnetic dipole part of the spin-spin

interaction,

$$\hat{H}_{\rm SO} = \frac{1}{2}\sum_{i=1}^{n_{\rm e}}\sum_{A=1}^{N_{\rm nuc}}\frac{Z_A}{r_{iA}^3}\hat{\boldsymbol{s}}_i\cdot\hat{\boldsymbol{l}}_{i,A}\ ,$$
$$\hat{H}_{\rm SOO} = -\frac{1}{2}\sum_{i=1}^{n_{\rm e}}\sum_{j=i+1}^{n_{\rm e}}\frac{1}{r_{ij}^3}\left[\hat{\boldsymbol{s}}_i\cdot\hat{\boldsymbol{l}}_{i,j}+\hat{\boldsymbol{s}}_j\cdot\hat{\boldsymbol{l}}_{j,i}\right]\ ,$$
$$\hat{H}_{\rm SOO'} = -\sum_{i=1}^{n_{\rm e}}\sum_{j=i+1}^{n_{\rm e}}\frac{1}{r_{ij}^3}\left[\hat{\boldsymbol{s}}_i\cdot\hat{\boldsymbol{l}}_{j,i}+\hat{\boldsymbol{s}}_j\cdot\hat{\boldsymbol{l}}_{i,j}\right]\ ,$$
$$\hat{H}_{\rm SS,dp} = \sum_{i=1}^{n_{\rm e}}\sum_{j=i+1}^{n_{\rm e}}\left[\frac{\hat{\boldsymbol{s}}_i\hat{\boldsymbol{s}}_j}{r_{ij}^3}-3\frac{(\hat{\boldsymbol{s}}_i\boldsymbol{r}_{ij})\,(\hat{\boldsymbol{s}}_j\boldsymbol{r}_{ij})}{r_{ij}^5}\right]\ , \tag{S12}$$

respectively, with $\hat{\boldsymbol{l}}_{a,b} = \boldsymbol{r}_{ab}\times\hat{\boldsymbol{p}}_a$.

The leading-order QED corrections to the spin-dependent couplings are due to the QED correction to the free-electron g factor, $g = 2\left[1+\frac{\alpha}{2\pi}+\mathcal{O}(\alpha^2)\right]$,

$$\alpha^3\hat{H}_{\rm sd}^{(3)} = \alpha^2\left[\frac{\alpha}{\pi}(\hat{H}_{\rm SO}+\hat{H}_{\rm SOO})+\frac{\alpha}{2\pi}\hat{H}_{\rm SOO'}+\frac{\alpha}{\pi}\hat{H}_{\rm SS,dp}\right]\ . \tag{S13}$$

S2. CONVERGENCE TABLES

The convergence of the b $^3\Pi_{\rm g}$ and c $^3\Sigma_{\rm g}^+$ electronic energy for $\rho = 2$ bohr internuclear distance is shown in Table S1. The table also reviews literature data and standard quantum chemistry computations (full configuration interaction, FCI) performed by us using the Molpro program package [9]. With standard approaches and basis sets near the 1 m$E_{\rm h}$ (10^{-3} $E_{\rm h}$) convergence of the electronic energy could be reached only with the (doubly and) triply augmented correlation consistent basis sets. Sub-m$E_{\rm h}$ convergence was easily reached with variationally optimised fECGs (already with $N_{\rm b} = 200$ optimised fECGs, which amounts to a few hours of computation on a PC). We also report the electronic energy for the d $^3\Sigma_{\rm u}^+$ and e $^3\Pi_{\rm g}$ (preliminary computations, providing upper bounds to the exact value) and compare it with available literature data for potential future relevance. In addition, small-scale fECG computations were also performed for the B $^1\Pi_{\rm g}$ and C $^1\Sigma_{\rm g}^+$ electronic states, for their significant spin-dependent relativistic couplings with the b and c states. The computational details and convergence for B and C are discussed in Ref. [4].

After the $\rho = 2$ bohr variational generation and optimisation of fECG basis sets, the PECs were generated by performing small consecutive displacements of $\Delta\rho = \pm 0.1$ bohr followed by the rescaling of the fECG centres and full reoptimization of the non-linear basis parameters [5, 10–12]. The consecutive rescaling and reoptimisation of the fECG parameterisation ensures that the local relative error of the PEC is smaller than the absolute convergence error of the total energy.

The convergence of the relativistic corrections for the b and c states is presented in Tables S2 and S3, respectively. In the rovibronic computations, we use the regularised values obtained with the numerical Drachmanization technique [3, 13], which we found to be more robust than the integral transformation (IT) technique [2, 8]. The relativistic corrections for the B and C states were also computed with the numerical Drachmanization approach. We only note that the C state is the first excited state in the $^1\Sigma_{\rm g}$ symmetry block, and this fact must be considered (use of the corresponding energy eigenvalue) in the Drachmanized expressions [3, 13]. The leading-order QED corrections are calculated using the Dirac-delta expectation values already computed for the relativistic corrections. We used the ion-core approximation for the Bethe logarithm, computed in Ref. [5], and tested its accuracy for the a $^3\Sigma_{\rm u}^+$ state in Ref. [7]. We computed the Araki-Sucher (AS) term for the c state in this work using the IT technique. The computation was repeated at all PEC points. The AS term provides a small correction to the energy (even smaller for relative rotational and vibrational intervals). We noticed that its value was very similar for the c and for the a states Ref. [7]. So, the b, B, and C leading-order QED corrections were computed using the AS correction curve taken from the c state (as a good approximation, considering the PEC error, etc.).

The convergence of the spin-dependent relativistic (and QED) couplings is discussed in detail in Ref. [4].

Table S4 shows convergence tests for the electronic angular momentum matrix elements, for the non-adiabatic and DBOC contributions. Table S5 shows the convergence of the electric dipole transition moment.

In the rovibronic computations, the $N_{\rm b} = 1000$ basis set of the b state was used for the PEC, DBOC and non-adiabatic couplings over the $\rho\in[1,10]$ bohr interval, whereas the relativistic corrections and couplings were computed

TABLE S1. Electronic energy, in E_h, for electronically excited states of He_2 ($\rho = 2$ bohr): b $^3\Pi_g$, c $^3\Sigma_g^+$, and pilot computations for d $^3\Sigma_u^+$, and e $^3\Pi_g$.

	U[b $^3\Pi_g$]	U[c $^3\Sigma_g^+$]	U[d $^3\Sigma_u^+$]	U[e $^3\Pi_g$]
MRCI [14, 15][a,b]	–5.123 5	–5.096 7		
MRCI [16][b]	–5.128 449	–		
MRCI [17][c]	–	–5.091		
FCI with Molpro [9] [this work]:				
FCI/aug-cc-pVDZ	–4.95	–5.04	–4.70	–4.25
FCI/aug-cc-pVTZ	–5.023	–5.081	–4.81	–4.38
FCI/aug-cc-pVQZ	–5.060	–5.088	–4.87	–4.46
FCI/aug-cc-pV5Z	–5.079	–5.091	–4.91	–4.51
FCI/daug-cc-pVDZ	–5.10	–5.076	–5.001	–4.83
FCI/daug-cc-pVTZ	–5.12	–5.095	–5.043 3	–4.88
FCI/daug-cc-pVQZ	–5.126	–5.098 6	–5.047 7	–4.925
FCI/daug-cc-pV5Z	–5.127 6	–5.099 76	–5.048 3	–4.953
FCI/taug-cc-pVDZ	–5.10	–5.076	–5.032	–5.027
FCI/taug-cc-pVTZ	–5.124	–5.095	–5.051 66	–5.043 5
FCI/taug-cc-pVQZ	–5.127 6	–5.098 9	–5.055 42	–5.047 2
FCI/taug-cc-pV5Z	–5.128 6	–5.099 8	–5.056 69	–5.049 4
R matrix [18]*	–5.124 7	–5.096 4	–5.055 19	–5.051 82
Variational ECG (QUANTEN) [this work]:[d]				
20	–5.11	–5.07		
50	–5.124	–5.093		
100	–5.127 9	–5.096 6		
200	–5.128 8	–5.099 6		
500	–5.129 25	–5.100 32		
750	–5.129 307[e]	–5.100 426		
1000	–5.129 329 6[e]	–5.100 464 7		
1250	–5.129 335 71	–5.100 475 59		–5.052 834 8[h]
1500	–5.129 339 08	–5.100 481 76[f,g]	–5.058 021 9[i]	
		–5.100 482 65		

[a] Ref. 18 reported relative values with respect to the a $^3\Sigma_u^+$ state energy from Ref. 14.
[b] Special basis set with diffuse functions.
[c] Extrapolated energy using aug-cc-pVnZ basis sets.
[d] The number of symmetry-adapted ECG functions (N_b) is listed in the first column.
[e] Basis sets used for PEC generation in this work.
[f] Obtained from the a $^3\Sigma_u^+$ parameterisation [7], after changing the symmetry, we have carried out several Powell refinement cycles of the entire basis set.
[g] This basis set was used for the c $^3\Sigma_g^+$ PEC generation in this work.
[h] Obtained from further optimization of the a $^3\Sigma_u^+$ $N_b = 1500$ (Ref. 7) basis set for the second electronic state.
[i] Obtained from further optimization of the b $^3\Pi_g$ $N_b = 1250$ basis set for the second electronic state.

with the $N_b = 750$ basis set also available for $\rho \in [1, 10]$ bohr. Regarding the c state, the PEC, all corrections curves and couplings were computed with the $N_b = 1500$ basis set of Table S1.

TABLE S2. b $^3\Pi_g$ He_2 ($\rho = 2$ bohr): Convergence of the relativistic corrections (in atomic units, to be multiplied by α^2), without regularisation (direct evaluation) and with the numerical Drachmanization approach [3].

N_b	$\langle \hat{H}_{MV} \rangle$	$\langle \hat{H}_{D1} \rangle$	$\langle \hat{H}_{D2} \rangle$	$\langle \hat{H}_{OO} \rangle$[a]	$\langle \hat{H}^{(2)}_{BP,sn} \rangle$
Direct evaluation:					
20	–21.406 904	17.462 862	–0.438 322	–0.042 397	–3.548 117
50	–22.165 453	18.118 236	–0.419 458	–0.033 837	–3.661 596
100	–22.850 082	18.743 318	–0.393 510	–0.031 681	–3.744 936
200	–23.001 121	18.876 257	–0.389 795	–0.030 917	–3.765 986
500	–23.106 521	18.976 478	–0.381 500	–0.030 285	–3.778 828
750	–23.359 460	19.208 785	–0.381 183	–0.030 207	–3.799 699
1000	–23.374 099	19.224 027	–0.378 770	–0.030 109	–3.801 411
Numerical Drachmann regularization:					
20	–23.378 789	19.342 105	–0.356 743	–	–3.722 338
50	–23.603 855	19.479 360	–0.363 593	–	–3.794 739
100	–23.709 769	19.551 920	–0.368 639	–	–3.820 891
200	–23.740 855	19.570 023	–0.369 879	–	–3.831 870
500	–23.753 778	19.580 085	–0.370 651	–	–3.833 327
750	–23.769 189	19.589 906	–0.370 724	–	–3.838 767
1000	–23.769 922	19.591 181	–0.370 840	–	–3.838 009

[a] The $\hat{H}_{OO}$ term is from direct computation; no regularisation is needed.

TABLE S3. c $^3\Sigma_g^+$ He_2 ($\rho = 2$ bohr): Convergence of the relativistic corrections (in atomic units), without regularisation, with the integral transformation (IT) technique [2, 8], and with the numerical Drachmanization approach [3].

N_b	$\langle \hat{H}_{MV} \rangle$	$\langle \hat{H}_{D1} \rangle$	$\langle \hat{H}_{D2} \rangle$	$\langle \hat{H}_{OO} \rangle$[a]	$\langle \hat{H}^{(2)}_{BP,sn} \rangle$
Direct evaluation:					
20	–20.671 326	16.780 649	–0.480 001	–0.068 849	–3.479 525
50	–22.289 192	18.196 139	–0.446 362	–0.081 569	–3.728 260
100	–23.320 502	19.100 363	–0.411 218	–0.081 292	–3.890 214
200	–23.562 205	19.336 949	–0.395 690	–0.079 879	–3.909 445
500	–23.849 102	19.595 722	–0.389 046	–0.079 479	–3.943 812
750	–23.894 195	19.644 650	–0.384 356	–0.079 314	–3.944 503
1000	–23.931 416	19.683 266	–0.382 466	–0.079 248	–3.944 932
1500	–24.085 349	19.828 320	–0.378 554	–0.079 177	–3.957 653
IT regularization:					
20	–21.139 961	16.946 048	–0.478 833	–	–3.783 930
50	–22.697 331	18.375 481	–0.445 276	–	–3.958 143
100	–23.764 766	19.293 970	–0.410 217	–	–4.141 872
200	–24.040 099	19.528 964	–0.394 727	–	–4.196 287
500	–24.131 601	19.772 173	–0.388 099	–	–4.050 808
750	–24.150 013	19.812 694	–0.383 420	–	–4.033 213
1000	–24.131 881	19.838 383	–0.381 531	–	–3.991 215
1500	–24.136 822	19.876 211	–0.377 673	–	–3.962 115
Numerical Drachamnn regularization:					
20	–23.381 989	19.362 670	–0.340 000	–	–3.748 169
50	–23.888 333	19.701 827	–0.364 112	–	–3.903 963
100	–24.061 962	19.823 630	–0.371 900	–	–3.947 724
200	–24.108 199	19.856 015	–0.374 515	–	–3.957 549
500	–24.132 984	19.872 447	–0.375 675	–	–3.964 342
750	–24.136 197	19.875 735	–0.376 032	–	–3.963 744
1000	–24.137 972	19.877 366	–0.376 132	–	–3.963 721
1500	–24.139 190	19.879 490	–0.376 230	–	–3.962 647

[a] The $\hat{H}_{OO}$ term is from direct computation, no regularization is needed.

TABLE S4. Convergence of the electronic angular momentum matrix elements with the basis size of the b and c states, N_b^b and N_b^c, respectively. The nuclei are on the z axis, the bra and the ket states have the same spin projection.

N_b^b	N_b^c	$\lvert\langle b^x \rvert \hat{L}_x \rvert c^0\rangle\rvert$	$\langle b^x \rvert \hat{L}_x^2 + \hat{L}_y^2 \rvert b^x\rangle$	$\langle c^0 \rvert \hat{L}_x^2 + \hat{L}_y^2 \rvert c^0\rangle$
Ref. [14]		0.863 897		
300	300	0.850 10	7.033 28	8.471 71
750	1000	0.850 73	7.036 46	8.468 97
1000	1500	0.850 79	7.036 65	8.469 06

TABLE S5. Convergence of the electronic dipole transition moments with the basis size of the b and c states, N_b^b and N_b^c, respectively. The nuclei are on the z axis, the bra and the ket states have the same spin projection. The basis set for the a state, with $N_b^a = 1500$, is taken from Ref. 7.

N_b	$\langle a^0 \rvert \mu_x \rvert b^x\rangle$	N_c	$\langle a^0 \rvert \mu_x \rvert c^0\rangle$
Ref. [14]	2.674 318		3.024 279
300	2.603 66	300	2.995 13
750	2.606 86	1000	2.994 12
1000	2.607 03	1500	2.994 08

TABLE S6. More comprehensive version of Table II: Computed c fine structure splittings, $\tilde{\nu}_{N\pm1} - \tilde{\nu}_N$ in cm^{-1} with the fully coupled b-c-B-C (bcBC) rovibronic model including non-adiabatic, relativistic (r) and QED couplings (Q). Deviation of the (±1) fine structure components, $\delta\nu^{\pm1}$ in MHz, from this bcBC(rQ) model obtained with bc(rQ): coupled b-c model with non-adiabatic, relativistic and QED couplings; bc(r): the coupled b-c model with non-adiabatic and relativistic couplings; and c(rQ): the single c-state model with relativistic and QED zero-field splitting.

	bcBC(rQ)		bc(rQ)		bc(r)		c(rQ)	
N	$\tilde{\nu}_{N-1} - \tilde{\nu}_N$	$\tilde{\nu}_{N+1} - \tilde{\nu}_N$	$\delta\nu^{-1}$	$\delta\nu^{+1}$	$\delta\nu^{-1}$	$\delta\nu^{+1}$	$\delta\nu^{-1}$	$\delta\nu^{+1}$
c, $v = 0$:								
0		0.020 234		–0.1		1.3		0
2	0.039 422	0.026 643	–0.1	–0.1	2.7	1.7	–34	18
4	0.033 102	0.028 839	–0.1	–0.1	2.3	1.8	–50	37
6	0.030 957	0.030 212	–0.1	–0.1	2.2	1.9	–68	55
8	0.029 659	0.031 288	–0.1	–0.1	2.1	1.9	–85	74
10	0.028 681	0.032 227	–0.1	–0.1	2.1	2.0	–103	93
c, $v = 1$:								
0		0.020 616		–0.1		1.4		0
2	0.040 179	0.027 149	–0.2	–0.1	2.7	1.7	–34	19
4	0.033 742	0.029 390	–0.1	–0.1	2.3	1.9	–51	37
6	0.031 562	0.030 794	–0.1	–0.1	2.2	1.9	–69	56
8	0.030 246	0.031 899	–0.1	–0.1	2.1	2.0	–87	76
10	0.029 258	0.032 865	–0.1	–0.1	2.1	2.0	–105	95
c, $v = 2$:								
0		0.021 066		–0.1		1.4		0
2	0.041 062	0.027 755	–0.2	–0.1	2.7	1.8	–35	19
4	0.034 481	0.030 080	–0.2	0.7	2.3	2.7	–52	39
6	0.032 254	0.031 496	–0.2	–0.3	2.2	1.8	–71	58
8	0.030 910	0.032 643	–0.2	–0.2	2.1	1.9	–90	78
10	0.029 902	0.033 653	–0.2	–0.2	2.1	1.9	–108	98
c, $v = 3$:								
0		0.021 575		0.0		1.5		0
2	0.042 034	0.028 451	–0.2	0.1	2.8	2.0	–36	21
4	0.035 328	0.030 827	1.3	0.1	3.8	2.2	–53	41
6	0.033 006	0.032 335	0.4	0.1	2.8	2.2	–73	62
8	0.031 625	0.033 538	0.3	0.1	2.7	2.3	–93	83
10	0.030 575	0.034 608	0.3	0.2	2.6	2.3	–113	104
c, $v = 4$:								
0		0.022 045		–0.1		1.5		0
2	0.042 891	0.029 123	–0.2	–0.1	2.9	1.9	–39	23
4	0.035 942	0.031 597	–0.2	–0.1	2.4	2.0	–59	45
6	0.033 546	0.033 185	–0.2	–0.1	2.3	2.1	–80	68
8	0.032 072	0.034 461	–0.2	0.0	2.2	2.2	–102	91
10	0.030 948	0.035 600	–0.2	0.0	2.2	2.2	–123	115

S3. SIMPLE CALCULATIONS FOR THE CARTESIAN AND THE SPHERICAL REPRESENTATIONS

The transition from the Cartesian to the spherical representation does not alter the Born-Oppenheimer (BO) and adiabatic energies of the states. The variational ECG computations were carried out in the $\mathcal{B}(xyz)$ Cartesian form in QUANTEN; however, for solving the rovibronic problem, it is more advantageous to use the spherical representation.

S3.1. Spherical vs. Cartesian relations for the orbital angular momentum couplings and corrections

In this section, we assume the identical Σ BF spin projection quantum number in the bra and in the ket unless explicitly stated otherwise.

$$\begin{aligned}
&\langle c|\hat{L}_a|c\rangle = 0\ , \quad \langle b^x|\hat{L}_a|b^x\rangle = 0\ , \quad \langle b^y|\hat{L}_a|b^y\rangle = 0\ , \quad a = x, y, z\\
&\langle b^x|\hat{L}_x|c\rangle = 0\ , \quad \langle b^x|\hat{L}_y|c\rangle = \mathrm{i}\eta\ (\eta \in \mathbb{R})\ , \quad \langle b^x|\hat{L}_z|c\rangle = 0\\
&\langle b^y|\hat{L}_y|c\rangle = 0\ , \quad \langle b^y|\hat{L}_x|c\rangle = -\mathrm{i}\eta\ (\eta \in \mathbb{R})\ , \quad \langle b^y|\hat{L}_z|c\rangle = 0
\end{aligned} \tag{S14}$$

$$\langle b^x|\hat{L}_z|b^y\rangle = -\mathrm{i} \quad \langle b^y|\hat{L}_z|b^x\rangle = +\mathrm{i} \tag{S15}$$

$$b^{\pm} = \frac{1}{\sqrt{2}}[b^x \pm \mathrm{i}b^y]\ . \tag{S16}$$

Then,

$$\begin{aligned}
\langle b^+|\hat{L}_z|b^+\rangle &= \frac{1}{2}\langle b^x + \mathrm{i}b^y|\hat{L}_z|b^x + \mathrm{i}b^y\rangle\\
&= \frac{1}{2}\left[\langle b^x|\hat{L}_z|b^x\rangle - \mathrm{i}\langle b^y|\hat{L}_z|b^x\rangle + \mathrm{i}\langle b^x|\hat{L}_z|b^y\rangle + \langle b^y|\hat{L}_z|b^y\rangle\right]\\
&= \frac{1}{2}\left[0 - \mathrm{i}\langle b^y|\hat{L}_z|b^x\rangle + \mathrm{i}\langle b^x|\hat{L}_z|b^y\rangle + 0\right] = 1
\end{aligned} \tag{S17}$$

$$\begin{aligned}
\langle b^-|\hat{L}_z|b^-\rangle &= \frac{1}{2}\langle b^x - \mathrm{i}b^y|\hat{L}_z|b^x - \mathrm{i}b^y\rangle\\
&= \frac{1}{2}\left[\langle b^x|\hat{L}_z|b^x\rangle + \mathrm{i}\langle b^y|\hat{L}_z|b^x\rangle - \mathrm{i}\langle b^x|\hat{L}_z|b^y\rangle + \langle b^y|\hat{L}_z|b^y\rangle\right]\\
&= \frac{1}{2}\left[0 - 1 - 1 + 0\right] = -1
\end{aligned} \tag{S18}$$

$$\begin{aligned}
\langle b^+|\hat{L}_z|b^-\rangle &= \frac{1}{2}\langle b^x - \mathrm{i}b^y|\hat{L}_z|b^x + \mathrm{i}b^y\rangle\\
&= \frac{1}{2}\left[0 + \mathrm{i}\langle b^y|\hat{L}_z|b^x\rangle + \mathrm{i}\langle b^x|\hat{L}_z|b^y\rangle - 0\right] = 0
\end{aligned} \tag{S19}$$

$$\langle b^-|\hat{L}_z|b^+\rangle = 0 \tag{S20}$$

$$\langle b^{\pm}|\boldsymbol{L}|b^{\pm}\rangle = \begin{pmatrix} 0\\ 0\\ \pm 1\end{pmatrix} \quad \text{and} \quad \langle b^{\pm}|\boldsymbol{L}|b^{\mp}\rangle = \begin{pmatrix} 0\\ 0\\ 0\end{pmatrix}\ . \tag{S21}$$

$$\langle b^x|\hat{L}_x|c\rangle = 0 \qquad \langle b^y|\hat{L}_y|c\rangle = 0 \tag{S22}$$

$$\langle b^x|\hat{L}_y|c\rangle = -\mathrm{i}\eta \qquad \langle b^y|\hat{L}_x|c\rangle = \mathrm{i}\eta \tag{S23}$$

$$\begin{aligned}\langle b^+|\hat{L}^+c\rangle = \frac{1}{\sqrt{2}}\langle b^x + \mathrm{i}b^y|[\hat{L}_x + \mathrm{i}\hat{L}_y]c\rangle &= \frac{1}{\sqrt{2}}[\langle b^x|\mathrm{i}\hat{L}_y|c\rangle - \mathrm{i}\langle b^y|\hat{L}_x|c\rangle] \\ &= \frac{1}{\sqrt{2}}[\mathrm{i}\langle b^x|\hat{L}_y|c\rangle - \mathrm{i}\langle b^y|\hat{L}_x|c\rangle] \\ &= \frac{1}{\sqrt{2}}[\mathrm{i}(-\mathrm{i})\eta - \mathrm{i}(\mathrm{i})\eta] = \sqrt{2}\eta\end{aligned} \tag{S24}$$

$$\begin{aligned}\langle b^+|\hat{L}_a^2|b^+\rangle &= \frac{1}{2}\langle b^x + \mathrm{i}b^y|\hat{L}_a^2|b^x + \mathrm{i}b^y\rangle \\ &= \frac{1}{2}[\langle b^x|\hat{L}_a^2|b^x\rangle - \mathrm{i}\langle b^y|\hat{L}_a^2|b^x\rangle + \mathrm{i}\langle b^x|\hat{L}_a^2|b^y\rangle + (-\mathrm{i})\mathrm{i}\langle b^y|\hat{L}_a^2|b^y\rangle] \\ &= \frac{1}{2}[\langle b^x|\hat{L}_a^2|b^x\rangle - 0 + 0 + \langle b^y|\hat{L}_a^2|b^y\rangle] \\ &= \frac{1}{2}[\langle b^x|\hat{L}_a^2|b^x\rangle + \langle b^y|\hat{L}_a^2|b^y\rangle]\end{aligned} \tag{S25}$$

$$\begin{aligned}\langle b^-|\hat{L}_a^2|b^-\rangle &= \frac{1}{2}\langle b^x - \mathrm{i}b^y|\hat{L}_a^2|b^x - \mathrm{i}b^y\rangle \\ &= \frac{1}{2}[\langle b^x|\hat{L}_a^2|b^x\rangle + \mathrm{i}\langle b^y|\hat{L}_a^2|b^x\rangle - \mathrm{i}\langle b^x|\hat{L}_a^2|b^y\rangle + \mathrm{i}(-\mathrm{i})\langle b^y|\hat{L}_a^2|b^y\rangle] \\ &= \frac{1}{2}[\langle b^x|\hat{L}_a^2|b^x\rangle - 0 + 0 + \langle b^y|\hat{L}_a^2|b^y\rangle] \\ &= \frac{1}{2}[\langle b^x|\hat{L}_a^2|b^x\rangle + \langle b^y|\hat{L}_a^2|b^y\rangle]\end{aligned} \tag{S26}$$

$$\begin{aligned}\langle b^+|\hat{L}_a^2|b^-\rangle &= \frac{1}{2}\langle b^x + \mathrm{i}b^y|\hat{L}_a^2|b^x - \mathrm{i}b^y\rangle \\ &= \frac{1}{2}[\langle b^x|\hat{L}_a^2|b^x\rangle - \mathrm{i}\langle b^y|\hat{L}_a^2|b^x\rangle - \mathrm{i}\langle b^x|\hat{L}_a^2|b^y\rangle + (-\mathrm{i})^2\langle b^y|\hat{L}_a^2|b^y\rangle] \\ &= \frac{1}{2}[\langle b^x|\hat{L}_a^2|b^x\rangle - \langle b^y|\hat{L}_a^2|b^y\rangle]\end{aligned} \tag{S27}$$

$$\begin{aligned}\langle b^-|\hat{L}_a^2|b^+\rangle &= \frac{1}{2}\langle b^x - \mathrm{i}b^y|\hat{L}_a^2|b^x + \mathrm{i}b^y\rangle \\ &= \frac{1}{2}[\langle b^x|\hat{L}_a^2|b^x\rangle + \mathrm{i}\langle b^y|\hat{L}_a^2|b^x\rangle + \mathrm{i}\langle b^x|\hat{L}_a^2|b^y\rangle + (\mathrm{i})^2\langle b^y|\hat{L}_a^2|b^y\rangle] \\ &= \frac{1}{2}[\langle b^x|\hat{L}_a^2|b^x\rangle - \langle b^y|\hat{L}_a^2|b^y\rangle]\end{aligned} \tag{S28}$$

Note: $\langle b^x|\hat{L}_x^2|b^x\rangle = \langle b^y|\hat{L}_y^2|b^y\rangle$, $\langle b^y|\hat{L}_x^2|b^y\rangle = \langle b^x|\hat{L}_y^2|b^x\rangle$, so

$$\langle b^+|\hat{L}_x^2 + \hat{L}_y^2|b^+\rangle = \langle b^-|\hat{L}_x^2 + \hat{L}_y^2|b^-\rangle = \langle b^x|\hat{L}_x^2 + \hat{L}_y^2|b^x\rangle = \langle b^y|\hat{L}_x^2 + \hat{L}_y^2|b^y\rangle \tag{S29}$$

$$\langle b^+|\hat{L}_x^2 + \hat{L}_y^2|b^-\rangle = \langle b^-|\hat{L}_x^2 + \hat{L}_y^2|b^+\rangle = 0 \tag{S30}$$

Similar relations apply for the B (and C) state components.

TABLE S7. $\mathcal{B}(xyz)$ Cartesian form of the non-vanishing relativistic QED couplings, $\beta_i, \gamma_i, \delta_i, \varepsilon_i (i = 1, 2), \lambda, \xi, \zeta \in \mathbb{R}$, within the bcBC electronic-spin subspace of He_2 as computed with QUANTEN. The Cartesian component of the spatial part and the Σ quantum number of the electron-spin part are in the superscript. The '.' labels zero (0). Note: $\beta_2 = -\beta_1/2$ and $\varepsilon_2 = -\varepsilon_1/2$; in Ref. 4, the $\beta_1 = \beta$ and $\varepsilon_1 = \varepsilon$ labelling is used.

	$b^{x,-1}$	$b^{x,0}$	$b^{x,1}$	$b^{y,-1}$	$b^{y,0}$	$b^{y,1}$	$c^{0,-1}$	$c^{0,0}$	$c^{0,1}$	$B^{x,0}$	$B^{y,0}$	$C^{0,0}$
$b^{x,-1}$	β_2	.	$-\gamma_1$	$-i\gamma_2$	.	$-i\gamma_1$	.	δ_2	.	.	.	λ
$b^{x,0}$	.	β_1	.	.	.	.	$-\delta_1$	.	δ_1	.	$i\zeta$	.
$b^{x,1}$	$-\gamma_1$	.	β_2	$i\gamma_1$	.	$i\gamma_2$	.	$-\delta_2$	.	.	.	λ
$b^{y,-1}$	$i\gamma_2$	.	$-i\gamma_1$	β_2	.	γ_1	.	$i\delta_2$	.	.	.	$i\lambda$
$b^{y,0}$	.	.	.	.	β_1	.	$i\delta_1$	.	$i\delta_1$	$-i\zeta$	.	.
$b^{y,1}$	$i\gamma_1$	.	$-i\gamma_2$	γ_1	.	β_2	.	$i\delta_2$	.	.	.	$-i\lambda$
$c^{0,-1}$	.	$-\delta_1$	.	.	$-i\delta_1$	.	ε_2	.	.	ξ	$i\xi$	.
$c^{0,0}$	δ_2	.	$-\delta_2$	$-i\delta_2$	.	$-i\delta_2$	.	ε_1	.	.	.	.
$c^{0,1}$	.	δ_1	.	.	$-i\delta_1$	.	.	.	ε_2	ξ	$-i\xi$	.
$B^{x,0}$	.	.	.	.	$i\zeta$	.	ξ	.	ξ	.	.	.
$B^{y,0}$	.	$-i\zeta$	.	.	.	.	$-i\xi$	.	$i\xi$	.	.	.
$C^{0,0}$	λ	.	λ	$-i\lambda$	.	$i\lambda$	.	.	.	.	.	.

TABLE S8. $\mathcal{B}(-1, 0, 1)$ spherical form of the relativistic QED, $\beta_i, \gamma_i, \varepsilon_i (i = 1, 2), \lambda, \xi, \zeta \in \mathbb{R}$ and non-adiabatic, $\eta, \kappa \in \mathbb{R}$ couplings of the bcBC electronic-spin subspace of He_2 used in the rovibronic computations. We also show the non-vanishing $\langle\varphi_{n'}|\hat{L}^+\varphi_n\rangle$ couplings (η, κ). All couplings are computed in the Cartesian representation with QUANTEN, the Cartesian to spherical transformation details are in the text. Please see also the caption to Table S7.

	$\|$ket$\rangle$	Λ	+1	+1	+1	−1	−1	−1	0	0	0	+1	−1	0
		Σ	−1	0	+1	−1	0	+1	−1	0	+1	0	0	0
$\langle$bra$\|$		Ω	0	+1	+2	−2	−1	0	−1	0	+1	+1	−1	0
Λ	Σ Ω		$b^{+,-}$	$b^{+,0}$	$b^{+,+}$	$b^{-,-}$	$b^{-,0}$	$b^{-,+}$	$c^{0,-}$	$c^{0,0}$	$c^{0,+}$	$B^{+,0}$	$B^{-,0}$	$C^{0,0}$
+1	−1 0	$b^{+,-}$	$\beta_2+\gamma_2$	.	.	.	.	$-2\gamma_1$	$\sqrt{2}\eta$	$\sqrt{2}\delta_2$	.	.	.	$\sqrt{2}\lambda$
+1	0 +1	$b^{+,0}$	.	β_1	.	.	.	.	.	$\sqrt{2}\eta$	$\sqrt{2}\delta_1$	$-\zeta$	.	.
+1	+1 +2	$b^{+,+}$	.	.	$\beta_2-\gamma_2$	.	.	.	.	.	$\sqrt{2}\eta$	.	.	.
−1	−1 −2	$b^{-,-}$	.	.	.	$\beta_2-\gamma_2$	.	.	$-\sqrt{2}\eta$	.	.	.	.	.
−1	0 −1	$b^{-,0}$	.	.	.	.	β_1	.	$-\sqrt{2}\delta_1$	$-\sqrt{2}\eta$	.	.	ζ	.
−1	+1 0	$b^{-,+}$	$-2\gamma_1$	.	.	.	.	$\beta_2+\gamma_2$	.	$-\sqrt{2}\delta_2$	$-\sqrt{2}\eta$	.	.	$\sqrt{2}\lambda$
0	−1 −1	$c^{0,-}$	$\sqrt{2}\eta$	.	.	$-\sqrt{2}\eta$	$-\sqrt{2}\delta_1$	.	ε_2	.	.	.	$\sqrt{2}\xi$	.
0	0 0	$c^{0,0}$	$\sqrt{2}\delta_2$	$\sqrt{2}\eta$	.	.	$-\sqrt{2}\eta$	$-\sqrt{2}\delta_2$	.	ε_1	.	.	.	.
0	+1 +1	$c^{0,+}$	.	$\sqrt{2}\delta_1$	$\sqrt{2}\eta$	.	.	$-\sqrt{2}\eta$	.	.	ε_2	$\sqrt{2}\xi$	.	.
+1	0 +1	$B^{+,0}$	.	$-\zeta$	.	.	.	.	.	.	$\sqrt{2}\xi$	.	.	$\sqrt{2}\kappa$
−1	0 −1	$B^{-,0}$	.	.	.	.	ζ	.	$\sqrt{2}\xi$	.	.	.	.	$-\sqrt{2}\kappa$
0	0 0	$C^{0,0}$	$\sqrt{2}\lambda$	.	.	.	.	$\sqrt{2}\lambda$	.	.	.	$\sqrt{2}\kappa$	$-\sqrt{2}\kappa$	.

S3.2. Spherical vs. Cartesian basis relations for the relativistic and QED couplings

In what follows $\hat{H}_{\rm rQ}$ labels the spin-dependent relativistic and/or leading-order QED operator, $\alpha^2\hat{H}^{(2)}_{\rm sd}$ or $\alpha^3\hat{H}^{(3)}_{\rm sd}$ or $\alpha^2\hat{H}^{(2)}_{\rm sd} + \alpha^3\hat{H}^{(3)}_{\rm sd}$. Furthermore, it is necessary to write out the BF spin projection quantum number (Σ) in this section. The non-vanishing coupling elements in the Cartesian basis representation (as computed with QUANTEN) are collected in Table S7.

$$\langle b^{x,\Sigma}|\hat{H}_{\rm rQ}|b^{x,\Sigma}\rangle = \langle b^{y,\Sigma}|\hat{H}_{\rm rQ}|b^{y,\Sigma}\rangle =: \beta\ , \quad \beta \in \mathbb{R} \tag{S31}$$

$$\langle b^{x,\Sigma}|\hat{H}_{\rm rQ}|b^{y,\Sigma}\rangle = -\langle b^{y,\Sigma}|\hat{H}_{\rm rQ}|b^{x,\Sigma}\rangle =: i\gamma\ , \quad \gamma \in \mathbb{R} \tag{S32}$$

$$
\begin{aligned}
&\langle \mathrm{b}^{\pm,\Sigma}|\hat{H}_{\mathrm{rQ}}|\mathrm{b}^{\pm,\Sigma}\rangle \\
&= \frac{1}{2}\langle \mathrm{b}^{x,\Sigma} \pm \mathrm{i}\mathrm{b}^{y,\Sigma}|\hat{H}_{\mathrm{rQ}}|\mathrm{b}^{x,\Sigma} \pm \mathrm{i}\mathrm{b}^{y,\Sigma}\rangle \\
&= \frac{1}{2}\left[\langle \mathrm{b}^{x,\Sigma}|\hat{H}_{\mathrm{rQ}}|\mathrm{b}^{x,\Sigma}\rangle + \langle \mathrm{b}^{y,\Sigma}|\hat{H}_{\mathrm{rQ}}|\mathrm{b}^{y,\Sigma}\rangle \pm \mathrm{i}\langle \mathrm{b}^{x,\Sigma}|\hat{H}_{\mathrm{rQ}}|\mathrm{b}^{y,\Sigma}\rangle \mp \mathrm{i}\langle \mathrm{b}^{y,\Sigma}|\hat{H}_{\mathrm{rQ}}|\mathrm{b}^{x,\Sigma}\rangle\right] \\
&= \frac{1}{2}\left[\beta + \beta \pm \mathrm{i}(\mathrm{i}\gamma) \mp \mathrm{i}(\mathrm{i}\gamma)^*\right] = \beta \mp \gamma \in \mathbb{R}
\end{aligned} \tag{S33}
$$

$$
\begin{aligned}
&\langle \mathrm{b}^{\mp,\Sigma}|\hat{H}_{\mathrm{rQ}}|\mathrm{b}^{\pm,\Sigma}\rangle \\
&= \frac{1}{2}\langle \mathrm{b}^{x,\Sigma} \mp \mathrm{i}\mathrm{b}^{y,\Sigma}|\hat{H}_{\mathrm{rQ}}|\mathrm{b}^{x,\Sigma} \pm \mathrm{i}\mathrm{b}^{y,\Sigma}\rangle \\
&= \frac{1}{2}\left[\langle \mathrm{b}^{x,\Sigma}|\hat{H}_{\mathrm{rQ}}|\mathrm{b}^{x,\Sigma}\rangle - \langle \mathrm{b}^{y,\Sigma}|\hat{H}_{\mathrm{rQ}}|\mathrm{b}^{y,\Sigma}\rangle \pm \mathrm{i}\langle \mathrm{b}^{x,\Sigma}|\hat{H}_{\mathrm{rQ}}|\mathrm{b}^{y,\Sigma}\rangle \pm \mathrm{i}\langle \mathrm{b}^{y,\Sigma}|\hat{H}_{\mathrm{rQ}}|\mathrm{b}^{x,\Sigma}\rangle\right] \\
&= \frac{1}{2}\left[\beta - \beta \pm \mathrm{i}(\mathrm{i}\gamma) \pm \mathrm{i}(\mathrm{i}\gamma)^*\right] = 0
\end{aligned} \tag{S34}
$$

We use the conventions introduced in the article, $\hat{O}_a$ ($a = x, y, z$) and $\hat{O}^{\pm}$ are BF operators.

$$
B^{+,\Sigma} = \frac{1}{\sqrt{2}}\left[B^{x,\Sigma} + \mathrm{i}B^{y,\Sigma}\right] \qquad B^{-,\Sigma} = \frac{1}{\sqrt{2}}\left[B^{x,\Sigma} - \mathrm{i}B^{y,\Sigma}\right] \tag{S35}
$$

$$
\langle b^{x,0}|\hat{H}_{\mathrm{rQ}}|B^{y,0}\rangle = \mathrm{i}\zeta \quad \text{and} \quad \langle b^{y,0}|\hat{H}_{\mathrm{rQ}}|B^{x,0}\rangle = -\mathrm{i}\zeta \tag{S36}
$$

In intermediate calculation steps, we drop the Σ superscript for brevity,

$$
\begin{aligned}
\langle b^{+,0}|\hat{H}_{\mathrm{rQ}}|B^{+,0}\rangle &= \frac{1}{2}\langle b^x + \mathrm{i}b^y|\hat{H}_{\mathrm{rQ}}|B^x + \mathrm{i}B^y\rangle \\
&= \frac{1}{2}[\langle b^x|\hat{H}_{\mathrm{rQ}}|B^x\rangle - \mathrm{i}\langle b^y|\hat{H}_{\mathrm{rQ}}|B^x\rangle + \mathrm{i}\langle b^x|\hat{H}_{\mathrm{rQ}}|B^y\rangle + \langle b^y|\hat{H}_{\mathrm{rQ}}|B^y\rangle] \\
&= \frac{1}{2}[0 - \zeta - \zeta + 0] = -\zeta
\end{aligned} \tag{S37}
$$

$$
\begin{aligned}
\langle b^{-,0}|\hat{H}_{\mathrm{rQ}}|B^{-,0}\rangle &= \frac{1}{2}\langle b^x - \mathrm{i}b^y|\hat{H}_{\mathrm{rQ}}|B^x - \mathrm{i}B^y\rangle \\
&= \frac{1}{2}[\langle b^x|\hat{H}_{\mathrm{rQ}}|B^x\rangle + \mathrm{i}\langle b^y|\hat{H}_{\mathrm{rQ}}|B^x\rangle - \mathrm{i}\langle b^x|\hat{H}_{\mathrm{rQ}}|B^y\rangle - \mathrm{i}^2\langle b^y|\hat{H}_{\mathrm{rQ}}|B^y\rangle] \\
&= \frac{1}{2}[0 - \mathrm{i}^2\zeta - \mathrm{i}^2\zeta + 0] = \zeta
\end{aligned} \tag{S38}
$$

$$
\begin{aligned}
\langle b^{+,0}|\hat{H}_{\mathrm{rQ}}|B^{-,0}\rangle &= \frac{1}{2}\langle b^x + \mathrm{i}b^y|\hat{H}_{\mathrm{rQ}}|B^x - \mathrm{i}B^y\rangle \\
&= \frac{1}{2}[\langle b^x|\hat{H}_{\mathrm{rQ}}|B^x\rangle - \mathrm{i}\langle b^y|\hat{H}_{\mathrm{rQ}}|B^x\rangle - \mathrm{i}\langle b^x|\hat{H}_{\mathrm{rQ}}|B^y\rangle - \mathrm{i}(-\mathrm{i})\langle b^y|\hat{H}_{\mathrm{rQ}}|B^y\rangle] \\
&= \frac{1}{2}[0 - \zeta + \zeta - 0] = 0
\end{aligned} \tag{S39}
$$

$$\begin{aligned}\langle b^{-,0}|\hat{H}_{\rm rQ}|B^{+,0}\rangle &= \frac{1}{2}\langle b^x - \mathrm{i}b^y|\hat{H}_{\rm rQ}|B^x + \mathrm{i}B^y\rangle \\ &= \frac{1}{2}[\langle b^x|\hat{H}_{\rm rQ}|B^x\rangle + \mathrm{i}\langle b^y|\hat{H}_{\rm rQ}|B^x\rangle + \mathrm{i}\langle b^x|\hat{H}_{\rm rQ}|B^y\rangle + \mathrm{i}^2\langle b^y|\hat{H}_{\rm rQ}|B^y\rangle] \\ &= \frac{1}{2}[0 - \mathrm{i}^2\zeta + \mathrm{i}^2\zeta + 0] = 0 \end{aligned} \tag{S40}$$

$$\langle b^{x,-}|\hat{H}_{\rm rQ}|C^{0,0}\rangle = \langle b^{x,+}|\hat{H}_{\rm rQ}|C^{0,0}\rangle = \lambda \tag{S41}$$

$$\langle b^{y,-}|\hat{H}_{\rm rQ}|C^{0,0}\rangle = \mathrm{i}\lambda \quad \text{and} \quad \langle b^{y,+}|\hat{H}_{\rm rQ}|C^{0,0}\rangle = -\mathrm{i}\lambda \tag{S42}$$

$$\langle b^{+,-}|\hat{H}_{\rm rQ}|C^{0,0}\rangle = \frac{1}{\sqrt{2}}[\langle b^{x,-}|\hat{H}_{\rm rQ}|C^{0,0}\rangle - \mathrm{i}\langle b^{y,-}|\hat{H}_{\rm rQ}|C^{0,0}\rangle] = \frac{1}{\sqrt{2}}[\lambda - \mathrm{i}^2\lambda] = \sqrt{2}\lambda \tag{S43}$$

$$\langle b^{+,+}|\hat{H}_{\rm rQ}|C^{0,0}\rangle = \frac{1}{\sqrt{2}}[\langle b^{x,+}|\hat{H}_{\rm rQ}|C^{0,0}\rangle - \mathrm{i}\langle b^{y,+}|\hat{H}_{\rm rQ}|C^{0,0}\rangle] = \frac{1}{\sqrt{2}}[\lambda + \mathrm{i}^2\lambda] = 0 \tag{S44}$$

$$\langle b^{-,-}|\hat{H}_{\rm rQ}|C^{0,0}\rangle = \frac{1}{\sqrt{2}}[\langle b^{x,-}|\hat{H}_{\rm rQ}|C^{0,0}\rangle + \mathrm{i}\langle b^{y,-}|\hat{H}_{\rm rQ}|C^{0,0}\rangle] = \frac{1}{\sqrt{2}}[\lambda + \mathrm{i}^2\lambda] = 0 \tag{S45}$$

$$\langle b^{-,+}|\hat{H}_{\rm rQ}|C^{0,0}\rangle = \frac{1}{\sqrt{2}}[\langle b^{x,+}|\hat{H}_{\rm rQ}|C^{0,0}\rangle + \mathrm{i}\langle b^{y,+}|\hat{H}_{\rm rQ}|C^{0,0}\rangle] = \frac{1}{\sqrt{2}}[\lambda - \mathrm{i}^2\lambda] = \sqrt{2}\lambda \tag{S46}$$

$$\langle c^{0,-}|\hat{H}_{\rm rQ}|B^{x,0}\rangle = \langle c^{0,+}|\hat{H}_{\rm rQ}|B^{x,0}\rangle = \xi \qquad \langle c^{0,-}|\hat{H}_{\rm rQ}|B^{y,0}\rangle = \mathrm{i}\xi \qquad \langle c^{0,+}|\hat{H}_{\rm rQ}|B^{y,0}\rangle = -\mathrm{i}\xi \tag{S47}$$

$$\begin{aligned}\langle c^{0,-}|\hat{H}_{\rm rQ}|B^{+,0}\rangle &= \frac{1}{\sqrt{2}}\langle c^{0,-}|\hat{H}_{\rm rQ}|B^{x,0} + \mathrm{i}B^{y,0}\rangle \\ &= \frac{1}{\sqrt{2}}[\langle c^{0,-}|\hat{H}_{\rm rQ}|B^{x,0}\rangle + \mathrm{i}\langle c^{0,-}|\hat{H}_{\rm rQ}|B^{y,0}\rangle] \\ &= \frac{1}{\sqrt{2}}[\xi + \mathrm{i}(\mathrm{i})\xi] = 0 \end{aligned} \tag{S48}$$

$$\begin{aligned}\langle c^{0,-}|\hat{H}_{\rm rQ}|B^{-,0}\rangle &= \frac{1}{\sqrt{2}}\langle c^{0,-}|\hat{H}_{\rm rQ}|B^{x,0} - \mathrm{i}B^{y,0}\rangle \\ &= \frac{1}{\sqrt{2}}[\langle c^{0,-}|\hat{H}_{\rm rQ}|B^{x,0}\rangle - \mathrm{i}\langle c^{0,-}|\hat{H}_{\rm rQ}|B^{y,0}\rangle] \\ &= \frac{1}{\sqrt{2}}[\xi - \mathrm{i}(\mathrm{i})\xi] = \sqrt{2}\xi \end{aligned} \tag{S49}$$

$$\begin{aligned}\langle c^{0,+}|\hat{H}_{\rm rQ}|B^{+,0}\rangle &= \frac{1}{\sqrt{2}}\langle c^{0,+}|\hat{H}_{\rm rQ}|B^{x,0} + \mathrm{i}B^{y,0}\rangle \\ &= \frac{1}{\sqrt{2}}[\langle c^{0,+}|\hat{H}_{\rm rQ}|B^{x,0}\rangle + \mathrm{i}\langle c^{0,+}|\hat{H}_{\rm rQ}|B^{y,0}\rangle] \\ &= \frac{1}{\sqrt{2}}[\xi + \mathrm{i}(-\mathrm{i})\xi] = \sqrt{2}\xi \end{aligned} \tag{S50}$$

$$\begin{aligned}\langle c^{0,+}|\hat{H}_{\mathrm{rQ}}|B^{-,0}\rangle &= \frac{1}{\sqrt{2}}\langle c^{0,+}|\hat{H}_{\mathrm{rQ}}|B^{x,0} - \mathrm{i}B^{y,0}\rangle \\ &= \frac{1}{\sqrt{2}}[\langle c^{0,+}|\hat{H}_{\mathrm{rQ}}|B^{x,0}\rangle - \mathrm{i}\langle c^{0,+}|\hat{H}_{\mathrm{rQ}}|B^{y,0}\rangle] \\ &= \frac{1}{\sqrt{2}}[\xi - \mathrm{i}(-\mathrm{i})\xi] = 0 \end{aligned} \tag{S51}$$

S4. AUXILIARY CALCULATIONS FOR THE COUPLED ROVIBRONIC EQUATION

$$\begin{aligned}\langle\varphi_{n'}\tilde{D}^J_{M_J\Omega'}|\boldsymbol{\Delta_\rho}|\varphi_n\tilde{D}^J_{M_J\Omega}\rangle\frac{1}{\rho}g_k = &\,\delta_{\Omega'\Omega}\langle\varphi_{n'}|\boldsymbol{\Delta_\rho}|\varphi_n\rangle\frac{1}{\rho}g_k + \delta_{n'n}\langle\tilde{D}^J_{M_J\Omega'}|\boldsymbol{\Delta_\rho}|\tilde{D}^J_{M_J\Omega}\rangle\frac{1}{\rho}g_k\\ &+\delta_{\Omega'\Omega}\delta_{n'n}\boldsymbol{\Delta_\rho}\left(\frac{1}{\rho}g_k\right) + 2\langle\varphi_{n'}|\boldsymbol{\nabla_\rho}|\varphi_n\rangle\langle\tilde{D}^J_{M_J\Omega'}|\boldsymbol{\nabla_\rho}|\tilde{D}^J_{M_J\Omega}\rangle\frac{1}{\rho}g_k\\ &+2\delta_{\Omega'\Omega}\langle\varphi_{n'}|\boldsymbol{\nabla_\rho}|\varphi_n\rangle\boldsymbol{\nabla_\rho}\left(\frac{1}{\rho}g_k\right)\\ &+2\delta_{n'n}\langle\tilde{D}^J_{M_J\Omega'}|\boldsymbol{\nabla_\rho}|\tilde{D}^J_{M_J\Omega}\rangle\boldsymbol{\nabla_\rho}\left(\frac{1}{\rho}g_k\right)\end{aligned} \tag{S52}$$

To evaluate the first three terms, we will use

$$\begin{aligned}\boldsymbol{\Delta_\rho} =&\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) - \frac{1}{\rho^2}\hat{R}^2 = \frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) - \frac{1}{\rho^2}(\hat{\boldsymbol{J}}-\hat{\boldsymbol{L}}-\hat{\boldsymbol{S}})^2\\ =&\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) - \frac{1}{\rho^2}\Big[(\hat{J}^2-J_z^2)+(\hat{L}_x^2+\hat{L}_y^2)+(\hat{S}^2-S_z^2)\\ &-(\hat{J}^+\hat{S}^- + \hat{J}^-\hat{S}^+) - (\hat{J}^+\hat{L}^- + \hat{J}^-\hat{L}^+) + (\hat{S}^+\hat{L}^- + \hat{S}^-\hat{L}^+)\Big]\,,\end{aligned} \tag{S53}$$

where we exploited that for the diatom's $\hat{\boldsymbol{R}}$ rotational angular momentum z component vanishes in the BF frame,

$$\begin{aligned}0 = \hat{R}_z^2 = (\hat{J}_z-\hat{L}_z-\hat{S}_z)^2 &= \hat{J}_z^2+\hat{L}_z^2+\hat{S}_z^2 - 2\hat{J}_z\hat{L}_z - 2\hat{J}_z\hat{S}_z + 2\hat{L}_z\hat{S}_z\\ \Rightarrow\;\; \hat{J}_z^2+\hat{L}_z^2+\hat{L}_z^2 &= 2\hat{J}_z\hat{L}_z + 2\hat{J}_z\hat{S}_z - 2\hat{L}_z\hat{S}_z\,,\end{aligned} \tag{S54}$$

and thus, we can write,

$$\begin{aligned}(\hat{\boldsymbol{J}}-\hat{\boldsymbol{L}}-\hat{\boldsymbol{S}})^2 =&\hat{J}^2+\hat{L}^2+\hat{S}^2 - 2\hat{\boldsymbol{J}}\cdot\hat{\boldsymbol{L}} - 2\hat{\boldsymbol{J}}\cdot\hat{\boldsymbol{S}} + 2\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\\ =&\hat{J}^2+\hat{L}_x^2+\hat{L}_y^2+\hat{L}_z^2+\hat{S}^2 - 2\hat{J}_z\hat{L}_z - 2\hat{J}_z\hat{S}_z + 2\hat{L}_z\hat{S}_z\\ &-2\hat{J}_x\hat{L}_x - 2\hat{J}_x\hat{S}_x + 2\hat{L}_x\hat{S}_x - 2\hat{J}_y\hat{L}_y - 2\hat{J}_y\hat{S}_y + 2\hat{L}_y\hat{S}_y\\ =&(\hat{J}^2-\hat{J}_z^2)+(\hat{L}_x^2+\hat{L}_y^2)+(\hat{S}^2-\hat{S}_z^2)\\ &-(\hat{J}^+\hat{S}^- + \hat{J}^-\hat{S}^+) - (\hat{J}^+\hat{L}^- + \hat{J}^-\hat{L}^+) + (\hat{S}^+\hat{L}^- + \hat{S}^-\hat{L}^+)\,.\end{aligned} \tag{S55}$$

For the last three terms of Eq. (S52), we can rely on the following relations,

$$\begin{aligned}\langle a'|\boldsymbol{\nabla_\rho}a\rangle\cdot\langle b'|\boldsymbol{\nabla_\rho}b\rangle &= \langle a'|\partial_\rho a\rangle\cdot\langle b'|\partial_\rho b\rangle - \frac{1}{\rho^2}\Big[\langle a'|\hat{R}_x a\rangle\cdot\langle b'|\hat{R}_x b\rangle + \langle a'|\hat{R}_y a\rangle\cdot\langle b'|\hat{R}_y b\rangle\Big]\\ &= \langle a'|\partial_\rho a\rangle\cdot\langle b'|\partial_\rho b\rangle - \frac{1}{\rho^2}\Big[\langle a'|(\hat{J}_x-\hat{L}_x-\hat{S}_x)a\rangle\cdot\langle b'|(\hat{J}_x-\hat{L}_x-\hat{S}_x)b\rangle\\ &+\langle a'|(\hat{J}_y-\hat{L}_y-\hat{S}_y)a\rangle\cdot\langle b'|(\hat{J}_y-\hat{L}_y-\hat{S}_y)b\rangle\Big]\\ &= \langle a'|\partial_\rho a\rangle\cdot\langle b'|\partial_\rho b\rangle - \frac{1}{2\rho^2}\Big[\langle a'|(\hat{J}^+-\hat{L}^+-\hat{S}^+)a\rangle\cdot\langle b'|(\hat{J}^--\hat{L}^--\hat{S}^-)b\rangle\\ &+\langle a'|(\hat{J}^--\hat{L}^--\hat{S}^-)a\rangle\cdot\langle b'|(\hat{J}^+-\hat{L}^+-\hat{S}^+)b\rangle\Big]\,,\end{aligned} \tag{S56}$$

where a and b can be any pairing of electronic, rotational, or vibrational functions, where $\hat{R}_z = 0$ was used.

Finally, we reiterate the action and matrix elements of the various angular momentum operators,

$$\hat{L}_z\varphi_n = \Lambda\varphi_n \quad \hat{S}_z\varphi_n = \Sigma\varphi_n \ , \quad \text{and} \quad \hat{S}^2\varphi_n = S(S+1)\varphi_n \ ,$$
$$\hat{J}_z\tilde{D}^J_{M_J\Omega} = \Omega\tilde{D}^J_{M_J\Omega} \ , \quad \hat{J}_Z\tilde{D}^J_{M_J\Omega} = M_J\tilde{D}^J_{M_J\Omega} \ , \quad \text{and} \quad \hat{J}^2\tilde{D}^J_{M_J\Omega} = J(J+1)\tilde{D}^J_{M_J\Omega} \ ,$$
$$\langle\tilde{D}^J_{M_J\Omega'}|\hat{J}^{\pm}\tilde{D}^J_{M_J\Omega}\rangle = \delta_{\Omega',\Omega\mp1}[J(J+1)-\Omega(\Omega\mp1)]^{\frac{1}{2}} = \delta_{\Omega',\Omega\mp1}C^{\mp}_{J\Omega} \ , \tag{S57}$$
$$\langle\varphi_{n'}|\hat{S}^{\pm}\varphi_n\rangle = \delta_{\Sigma',\Sigma\pm1}[S(S+1)-\Sigma(\Sigma\pm1)]^{\frac{1}{2}} = \delta_{\Sigma',\Sigma\pm1}C^{\pm}_{S\Sigma} \ , \tag{S58}$$

with $\langle\varphi_{n'}|\hat{L}^{\pm}\varphi_n\rangle$ computed numerically, and we note that $\frac{\partial}{\partial\rho}|\tilde{D}^J_{M_J\Omega}\rangle = 0$. So, we can proceed with the evaluation of each term in Eq. (S52) as

$$\begin{aligned}\langle\varphi_{n'}|\boldsymbol{\Delta_\rho}|\varphi_n\rangle &= \langle\varphi_{n'}|\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right)|\varphi_n\rangle - \frac{1}{\rho^2}\langle\varphi_{n'}|(\hat{L}_x^2+\hat{L}_y^2)+(\hat{S}^2-S_z^2)|\varphi_n\rangle \\ &- \frac{1}{\rho^2}\langle\varphi_{n'}|(\hat{S}^+\hat{L}^- + \hat{S}^-\hat{L}^+)\varphi_n\rangle \\ &= -\langle\frac{\partial}{\partial\rho}\varphi_{n'}|\frac{\partial}{\partial\rho}\varphi_n\rangle - \frac{1}{\rho^2}\langle\varphi_{n'}|\hat{L}_x^2+\hat{L}_y^2|\varphi_n\rangle - \delta_{n'n}\frac{1}{\rho^2}[S(S+1)-\Sigma^2] \\ &- \frac{1}{\rho^2}\left[\delta_{\Lambda'\Lambda+1}\delta_{\Sigma'\Sigma+1}C^+_{S\Sigma}\langle\varphi_{n'}|\hat{L}^+\varphi_n\rangle + \delta_{\Lambda'\Lambda-1}\delta_{\Sigma'\Sigma-1}C^-_{S\Sigma}\langle\varphi_{n'}|\hat{L}^-\varphi_n\rangle\right]\end{aligned} \tag{S59}$$

$$\langle\tilde{D}^J_{M_J\Omega'}|\boldsymbol{\Delta_\rho}|\tilde{D}^J_{M_J\Omega}\rangle = -\frac{1}{\rho^2}\langle\tilde{D}^J_{M_J\Omega'}|\hat{J}^2-\hat{J}_z^2|\tilde{D}^J_{M_J\Omega}\rangle = -\frac{1}{\rho^2}\delta_{\Omega'\Omega}[J(J+1)-\Omega^2] \tag{S60}$$

$$\boldsymbol{\Delta_\rho}\left(\frac{1}{\rho}g_k\right) = \frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right)\left[\frac{1}{\rho}g_k\right] = \frac{1}{\rho}\frac{\partial^2 g_k}{\partial\rho^2} \tag{S61}$$

$$\begin{aligned}2\langle\varphi_{n'}|\boldsymbol{\nabla_\rho}\varphi_n\rangle\langle\tilde{D}^J_{M_J\Omega'}|\boldsymbol{\nabla_\rho}\tilde{D}^J_{M_J\Omega}\rangle &= \frac{1}{\rho^2}\langle\varphi_{n'}|(\hat{S}^+ + \hat{L}^+)\varphi_n\rangle\langle\tilde{D}^J_{M_J\Omega'}|\hat{J}^-\tilde{D}^J_{M_J\Omega}\rangle \\ &+ \frac{1}{\rho^2}\langle\varphi_{n'}|(\hat{S}^- + \hat{L}^-)\varphi_n\rangle\langle\tilde{D}^J_{M_J\Omega'}|\hat{J}^+\tilde{D}^J_{M_J\Omega}\rangle \\ &= \frac{1}{\rho^2}\Big[\delta_{\Lambda'\Lambda}\delta_{\Sigma'\Sigma+1}C^+_{J\Omega}C^+_{S\Sigma} + \delta_{\Lambda'\Lambda+1}\delta_{\Sigma'\Sigma}C^+_{J\Omega}\langle\varphi_n|\hat{L}^+\varphi_{n'}\rangle \\ &+ \delta_{\Lambda'\Lambda}\delta_{\Sigma'\Sigma-1}C^-_{J\Omega}C^-_{S\Sigma} + \delta_{\Lambda'\Lambda-1}\delta_{\Sigma'\Sigma}C^-_{J\Omega}\langle\varphi_n|\hat{L}^-\varphi_{n'}\rangle\Big]\end{aligned} \tag{S62}$$

$$2\langle\varphi_{n'}|\boldsymbol{\nabla_\rho}\varphi_n\rangle\boldsymbol{\nabla_\rho}\left(\frac{1}{\rho}g_k\right) = 2\langle\varphi_{n'}|\frac{\partial}{\partial\rho}\varphi_n\rangle\cdot\frac{\partial}{\partial\rho}\left(\frac{1}{\rho}g_k\right) \tag{S63}$$

$$2\langle\tilde{D}^J_{M_J\Omega'}|\boldsymbol{\nabla_\rho}\tilde{D}^J_{M_J\Omega}\rangle\boldsymbol{\nabla_\rho}\left(\frac{1}{\rho}g_k\right) = 0 \tag{S64}$$

By noting that Eq. (S63) vanishes for the b $^3\Pi_g$ and c $^3\Sigma_g^+$ states, we arrive at the coupled radial equation.

$$\begin{aligned}\boldsymbol{\Delta_\rho} &= \frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) - \frac{1}{\rho^2}\hat{\boldsymbol{R}}^2 \\ &= \frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) \\ &- \frac{1}{\rho^2}\Big[(\hat{N}^2-N_z^2)+(\hat{L}_x^2+\hat{L}_y^2)-(N^+L^-+N^-L^+)\Big] \ .\end{aligned} \tag{S65}$$

[1] P. J. Mohr, D. B. Newell, B. N. Taylor, and E. Tiesinga, CODATA recommended values of the fundamental physical constants: 2022, Rev. Mod. Phys. **97**, 025002 (2025).

[2] P. Jeszenszki, R. T. Ireland, D. Ferenc, and E. Mátyus, On the inclusion of cusp effects in expectation values with explicitly correlated Gaussians, Int. J. Quant. Chem. **122**, e26819 (2022).

[3] B. Rácsai, D. Ferenc, A. Margócsy, and E. Mátyus, Regularized relativistic corrections for polyelectronic and polyatomic systems with explicitly correlated Gaussians, J. Chem. Phys. **160**, 211102 (2024).

[4] P. Jeszenszki, P. Hollósy, Á. Margócsy, and E. Mátyus, Spin-dependent terms of the Breit-Pauli Hamiltonian evaluated with explicitly correlated Gaussian basis set for molecular computations, arXiv:2506.19131 .

[5] D. Ferenc, V. I. Korobov, and E. Mátyus, Nonadiabatic, relativistic, and leading-order QED corrections for rovibrational intervals of $^4\mathrm{He}_2^+$ ($X\ ^2\Sigma_u^+$), Phys. Rev. Lett. **125**, 213001 (2020).

[6] D. Ferenc and E. Mátyus, Evaluation of the Bethe logarithm: From atom to chemical reaction, J. Phys. Chem. A **127**, 627 (2023).

[7] Á. Margócsy, B. Rácsai, P. Jeszenszki, and E. Mátyus, Rovibrational computations for the He_2 a $^3\Sigma_\mathrm{u}^+$ state including non-adiabatic, relativistic, and QED corrections, arXiv:2506.19116 .

[8] K. Pachucki, W. Cencek, and J. Komasa, On the acceleration of the convergence of singular operators in Gaussian basis sets, J. Chem. Phys. **122**, 184101 (2005).

[9] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, Molpro: a general-purpose quantum chemistry program package, WIREs Comp. Mol. Sci. **2**, 242 (2012).

[10] W. Cencek and J. Rychlewski, Many-electron explicitly correlated Gaussian functions. II. Ground state of the helium molecular ion He_2^+, J. Chem. Phys. **102**, 2533 (1995).

[11] D. Ferenc and E. Mátyus, Non-adiabatic mass correction for excited states of molecular hydrogen: Improvement for the outer-well $H\bar{H}\ ^1\Sigma_g^+$ term values, J. Chem. Phys. **151**, 094101 (2019).

[12] D. Ferenc and E. Mátyus, Benchmark potential energy curve for collinear H_3, Chem. Phys. Lett. **801**, 139734 (2022).

[13] R. Drachman, A new global operator for two-particle delta functions, J. Phys. B: At. Mol. Opt. Phys. **14**, 2733 (1981).

[14] D. R. Yarkony, On the quenching of helium 2 ^3S: Potential energy curves for, and nonadiabatic, relativistic, and radiative couplings between, the $a\ ^3\Sigma_\mathrm{u}^+$, $A\ ^1\Sigma_\mathrm{u}^+$, $b\ ^3\Pi_\mathrm{g}$, $B\ ^1\Pi_\mathrm{g}$, $c\ ^3\Sigma_\mathrm{g}^+$, and $C\ ^1\Sigma_\mathrm{g}^+$ states of He_2, J. Chem. Phys. **90**, 7164 (1989).

[15] C. F. Chabalowski, J. O. Jensen, D. R. Yarkony, and B. H. Lengsfield, Theoretical study of the radiative lifetime for the spin-forbidden transition $a\ ^3\Sigma_\mathrm{u}^+ \to X\ ^1\Sigma_\mathrm{g}^+$ in He_2, J. Chem. Phys. **90**, 2504 (1989).

[16] N. Bjerre, A. O. Mitrushenkov, P. Palmieri, and P. Rosmus, Spin-orbit and spin-spin couplings in He_2 and He_2^-, Theor. Chem. Acc. **100**, 51 (1998).

[17] S. Xu, A. Lu, X. Zhong, Y. Guo, and J. Shi, Ab initio investigation of potential energy curves of He_2, He_2^+, and extrapolation by the machine learning method, Int. J. Quant. Chem. **124**, e27367 (2024).

[18] M. D. E. Epée, O. Motapon, K. Chakrabarti, and J. Tennyson, Theoretical investigation of Rydberg states of He_2 using the R-matrix method, Mol. Phys. **122**, e2295013 (2024).