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Precision calculations for three-body molecular bound states

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Abstract. Although they do not lend themselves to analytical resolution, three-body atomic or molecular systems are still simple enough to allow for very precise theoretical predictions of their energy levels, which makes them attractive candidates for fundamental tests and determination of fundamental physical constants. Focusing on the hydrogen molecular ions (H_2^+ , HD^+ , D_2^+), we outline the methods which have been used to improve the theoretical accuracy by several orders of magnitude over the last two decades. The three-body Schrödinger equation can be solved with extreme precision by variational methods with trial functions involving exponentials of interparticle distances. Quantum electrodynamics (QED) corrections are evaluated in the framework of nonrelativistic QED (NRQED). The current status of theory and possibilities of further improvement are briefly sketched.

Keywords: Three-body Coulomb problem, bound states, hydrogen molecular ions, variational methods, QED corrections, NRQED, fundamental constants

1 Introduction

Precision spectroscopy of two-body (hydrogenlike) atoms, combined with QED calculations of their energy levels, has been a very successful way to test fundamental physics at a low-energy scale and has led to precise determinations of the Rydberg constant and proton charge radius [1]. In the last decade, the still unresolved discrepancy between results from H spectroscopy [2,3], muonic hydrogen spectroscopy [4], and electron-proton scattering experiments [5], known as the "proton-radius puzzle", has been a subject of intense activity. Three-body atoms or molecules have rich potential for further investigations in this field. Although theoretically more complex, they can have experimentally favorable features like

the existence of narrow transitions, and can be sensitive to different physics or fundamental constants. For example, spectroscopy of antiprotonic helium has been used to determine the antiproton-to-electron mass ratio and test the CPT symmetry [6], and experiments in pionic helium [7] are underway to determine the charged pion mass. Measurements in He have recently allowed extracting the ${}^3\text{He}$ - ${}^4\text{He}$ nuclear charge radius difference [8,9], to be compared with the value deduced from muonic helium spectroscopy [10]; future theoretical progress would allow extraction of individual radii [11]. Spectroscopy of ro-vibrational transitions in the hydrogen molecular ions (HMI), H_2^+ and its isotopes HD^+ and D_2^+ , can be used for determination of the proton-electron and deuteron-electron mass ratios [12,13,14], and, if an appropriate set of transitions is measured, of the proton and deuteron charge radii and Rydberg constant [15]. Measurements in the antihydrogen molecular ion $\bar{\text{H}}_2^-$ compared with its normal matter counterpart have also been proposed for improved CPT symmetry tests [16].

The main purpose of this paper is to introduce the reader to the theoretical methods used to calculate the energy levels of three-body Coulomb bound states with very high accuracy, with emphasis on the case of HMI. The first part is devoted to the Schrödinger equation and its resolution by variational methods, and the second part deals with the calculation of QED corrections. An outline of the NRQED approach is given, after which the current status of theoretical predictions in HMI and perspectives of further improvement are briefly discussed.

2 Variational solutions of the Schrödinger equation

HMI play the role of benchmark systems in quantum chemistry, and the calculation of their nonrelativistic energy levels have been studied in hundreds of theoretical papers. Calculations were initially performed in the framework of the Born-Oppenheimer approximation; nonadiabatic calculations appeared in the 1970s [17], motivated by the first precise spectroscopic measurements in HD^+ [18]. Since then, refinements in theoretical methods and constant increase of available computing power have allowed improving the precision by many orders of magnitude, as illustrated in Table 1 for the ground-state energy of H_2^+ . A majority of the most accurate results have been obtained using the variational approach and different variants of "exponential" basis sets [19,20,21,22,23], which we will now present.

Let us consider a rovibrational state of a HMI supported by the ground $1s_g$ electronic curve. Its total spatial parity is $\Pi = (-1)^L$ where L is the rotational quantum number. The wavefunction ψ_{LM}^{Π} of such a state may be written using the following separation of angular and radial degrees of freedom [24]:

$$\psi_{LM}^{\Pi}(\mathbf{R}, \mathbf{r}_1) = \sum_{l_1+l_2=L} \mathcal{Y}_{LM}^{l_1 l_2}(\mathbf{R}, \mathbf{r}_1) G_{l_1 l_2}^{L\Pi}(R, r_1, r_2), \quad (1)$$

$$\mathcal{Y}_{LM}^{l_1 l_2}(\mathbf{R}, \mathbf{r}_1) = r_1^{l_1} r_2^{l_2} \{Y_{l_1} \otimes Y_{l_2}\}_{LM}. \quad (2)$$

Here, \mathbf{r}_i ($i = 1, 2$) is the position of the electron with respect to nucleus i , and $\mathbf{R} = \mathbf{r}_1 - \mathbf{r}_2$ is the internuclear vector. The radial functions $G_{l_1 l_2}^{L\Pi}(R, r_1, r_2)$ are

Table 1. Selected theoretical results for the nonrelativistic energy of the H_2^+ ground state (i.e. the $(v = 0, L = 0)$ rovibrational state supported by the $1s\sigma_g$ electronic curve). The CODATA 1986 value of the mass ratio, $m_p/m_e = 1836.152701$, was used in all works excepted for Ref. [17] where $m_e/m_p = 5.44617 \cdot 10^{-4}$. N is the number of terms in the expansion of the wave function. Stars signal cases where the eigenvalue problem in Eq. (6) involves sparse-band matrices, which greatly reduces its complexity.

Author (year)	Ref.	Method	N	Energy (a.u.)
Bishop (1977)	[17]	Var. elliptic	515	-0.597 139 062 5
Moss (1993)	[25]	Transformed H		-0.597 139 063 12(5)
Grémaud (1998)	[26]	Var. perimetric	31746*	-0.597 139 063 123(1)
Moss (1999)	[27]	Var. elliptic		-0.597 139 063 123 4(1)
Hilico (2000)	[28]	Var. perimetric	66046*	-0.597 139 063 123 40(1)
Korobov (2000)	[19]	Var. exponential	2200	-0.597 139 063 123 405 074
Bailey (2002)	[20]	Var. exponential	3500	-0.597 139 063 123 405 074 83
Cassar (2004)	[21]	Var. exponential	1052	-0.597 139 063 123 405 074 834 338(3)
Li (2007)	[22]	Var. exponential	8381	-0.597 139 063 123 405 074 834 134 096 026(5)
Hijikata (2009)	[29]	Free complement	19286	-0.597 139 063 123 405 074 834 134 096 026 0
Ning (2014)	[23]	Var. exponential	3806	-0.597 139 063 123 405 074 834 134 096 026 189 9(1)

then expanded in a basis set involving exponentials of inter-particle distances. Two different types of expansion have been used with particular success. The first one uses pure exponential functions [19,20]:

$$G_{l_1 l_2}^{L\Pi}(R, r_1, r_2) = \sum_{n=1}^{N_{l_2}} [C_n \text{Re}(e^{-\alpha_n R - \beta_n r_1 - \gamma_n r_2}) + D_n \text{Im}(e^{-\alpha_n R - \beta_n r_1 - \gamma_n r_2})] \quad (3)$$

where the exponents $\alpha_n, \beta_n, \gamma_n$ are complex numbers. In practice, it is essential to use complex α_n in order to reproduce the oscillatory behavior of the vibrational part of the wavefunction, but β_n and γ_n can be kept real. The real and imaginary parts of exponents are generated pseudo-randomly in several intervals, the bounds of which play the role of variational parameters and need to be optimized. The second type of expansion is [21,23,30]

$$G_{l_1 l_2}^{L\Pi}(R, r_1, r_2) = \sum_{p=1}^2 \sum_{i,j=0}^{\Omega} \sum_{k=\Omega_{\text{low}}}^{\Omega_{\text{high}}} C_{ijk}^{(p)} r_1^i r_2^j R^k e^{-\alpha_p R - \beta_p r_1 - \gamma_p r_2} \quad (4)$$

where all exponents are real, and their values are fully optimized through calculation of the first derivatives of the energy with respect to $\alpha_p, \beta_p, \gamma_p$.

According to the basic variational theorem, the quantity

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \quad (5)$$

provides an upper bound for the exact ground-state energy E_0 . Finding the extrema of E with respect to the linear parameters (C_n, D_n in Eq. (3) or $C_{ijk}^{(p)}$

in Eq. (4) is equivalent to solving the generalized eigenvalue problem

$$\mathbf{A}c = \lambda\mathbf{B}c \quad (6)$$

where c is a column vector of coefficients ($\psi = \sum_{i=1}^N c_i \psi_i$), \mathbf{A} the Hamiltonian matrix ($A_{ij} = \langle \psi_i | H | \psi_j \rangle$), and \mathbf{B} the overlap matrix ($B_{ij} = \langle \psi_i | \psi_j \rangle$). The lowest eigenvalue λ_0 is an upper bound to E_0 ; a less widely known property called the Hylleraas-Undheim-MacDonald theorem [31,32], crucial for the applicability of variational methods to excited states, is that the other eigenvalues $\lambda_1, \lambda_2 \dots$ are also upper bounds to the exact energies $E_1, E_2 \dots$.

An essential property of the above "exponential" expansions allowing to get high-precision results is that the matrix elements of the Hamiltonian, as well as those appearing in calculation of relativistic and QED corrections, can be evaluated analytically [30,33,34].

The efficiency of variational methods is not limited to the first few excited states, contrary to a common misconception. For example, in the recent work [35], the energies of all bound and quasibound states of H_2^+ supported by the $1s\sigma_g$ electronic curve were calculated with an uncertainty of 10^{-7} cm^{-1} , using the complex coordinate rotation method for quasibound states. An important technical point is that the quasi-adiabaticity of HMI greatly helps reducing the complexity of the calculation for high rotational states as it allows restricting the sum in Eq. (1) to low values of l_2 (which is related to the electronic orbital momentum).

One may wonder what kind of accuracy is actually required for fundamental metrology applications. Typically, an uncertainty of 10^{-20} a.u. on the nonrelativistic energy level allows calculation of leading-order (α^2) corrections with 10 significant digits, and with an absolute uncertainty $< 10^{-14}$ a.u. The resulting relative uncertainty on rovibrational transition frequencies ($\nu \sim 0.01$ a.u.) is $< 10^{-12}$, which is still smaller than the uncertainty from unevaluated high-order QED corrections (see next Section). Since such (or even better) accuracies can be obtained with modest computing resources, the nonrelativistic three-body bound-state problem may be regarded as solved from a practical viewpoint.

3 Calculation of QED corrections

We now give a basic introduction to nonrelativistic quantum electrodynamics (NRQED) and its application to HMI. The NRQED approach, originally proposed by Caswell and Lepage [36] and further developed by other authors (see e.g. [37,38,39]) is a powerful tool to study QED corrections in weakly bound few-body systems. In brief, it consists in constructing from QED a nonrelativistic Lagrangian describing the interaction of an electron or a nucleus with the electromagnetic field, and then using it to calculate the QED corrections by applying the nonrelativistic perturbation theory. One way of constructing the NRQED Lagrangian [36,37] is to write all possible interactions satisfying the required symmetries, such as gauge invariance, parity invariance, time reversal,

Galilean invariance, hermiticity, and locality. In principle this is an infinite expansion, but it may be truncated according to the order of the correction one wants to calculate. Its first few terms are

$$\mathcal{L} = \psi^\dagger \left\{ iD_t + \frac{\mathbf{D}^2}{2m} + \frac{\mathbf{D}^4}{8m^3} + c_F q \frac{\boldsymbol{\sigma} \cdot \mathbf{B}}{2m} + c_D q \frac{\boldsymbol{\nabla} \cdot \mathbf{E}}{8m^2} + i c_S q \frac{\boldsymbol{\sigma} \cdot (\mathbf{D} \times \mathbf{E} - \mathbf{E} \times \mathbf{D})}{8m^2} \right\} \psi \quad (7)$$

where q, m are the particle's mass and charge, $D_t = \partial_t + iqA_0$, and $\mathbf{D} = \boldsymbol{\nabla} - iq\mathbf{A}$.

The coefficients of this Lagrangian are regularized by introducing a cutoff on the photon momentum of the order of the electron's rest energy. Physics at relativistic energy scales is incorporated in the theory in the form of contact terms. Finally, the coefficients of the Lagrangian are fixed by imposing that the NRQED and QED scattering amplitudes coincide up to the desired order - this is the so-called "matching" procedure. An alternative approach [38,39] is to obtain the NRQED Hamiltonian directly from the Dirac Hamiltonian through a Foldy-Wouthuysen transformation.

It is important to note that the matching is the only stage of the method which involves calculation of QED diagrams. It is done using only the scattering of free particles, and does not involve any bound states. This separation of the matching from the bound-state calculations is a key simplification allowed by the NRQED approach.

After the Lagrangian has been constructed, the next step is to apply the nonrelativistic perturbation theory. This can be formalized in terms of NRQED Feynman rules similarly to QED (see Fig. 3 in [37]). The number of interaction vertices is much higher than in QED since there are many terms in the NRQED Lagrangian, but each diagram is much simpler to calculate. To illustrate this procedure, all diagrams contributing to the leading-order (Breit-Pauli) hyperfine Hamiltonian of HMI are shown in Fig. 1. The interaction potential corresponding to each diagram is directly obtained in impulse space through application of NRQED Feynman rules, and Fourier transform gives the potentials in coordinate space (see Eq. (2) of [40]).

Application of the NRQED approach to HMI has allowed calculation of leading-order relativistic and radiative corrections at the $m\alpha^4$ and $m\alpha^5$ orders [42]. Among these, the most difficult contribution to evaluate is the Bethe logarithm, which may be expressed as a sum over intermediate states converging very slowly as the maximal energy of the states included in the sum is increased. Its evaluation therefore requires an accurate representation of scattering states lying high in the continuum. An efficient numerical scheme for calculating the Bethe logarithm is presented in Ref. [43].

Corrections of order $m\alpha^6$, $m\alpha^7$, and (partially) $m\alpha^8$ have been calculated in the framework of the adiabatic approximation [44,45,46], including only corrections to the bound electron in a two-center potential. Spin-averaged rovibrational transition frequencies are now predicted with a relative uncertainty of $7.6 \cdot 10^{-12}$ [46], which already allows for an improved determination of the proton-electron mass ratio if a measurement of similar accuracy is performed in ongoing Doppler-free spectroscopy experiments. Further progress in accuracy by

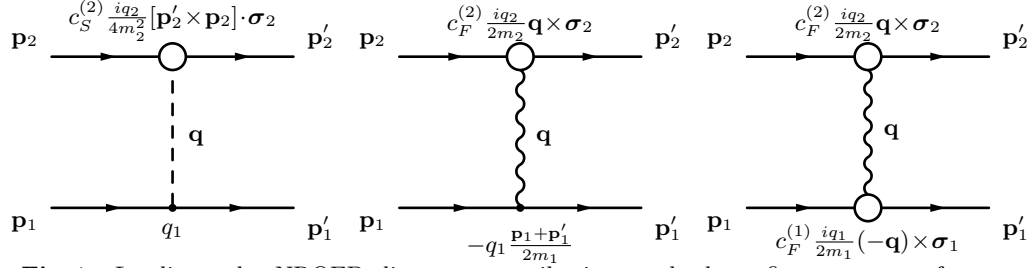


Fig. 1. Leading-order NRQED diagrams contributing to the hyperfine structure of HMI. Particles 1 and 2 may be either an electron or one of the nuclei. Left: Coulomb photon exchange (dashed line) where 1 and 2 respectively interact via Coulomb and spin-orbit vertices. Center: transverse photon exchange (wiggly line) where 1 and 2 interact via dipole and Fermi vertices. Right: transverse photon exchange where both particles interact via a Fermi vertex. The photon impulse is $\mathbf{q} = \mathbf{p}'_2 - \mathbf{p}_2$. The matching with QED yields $c_F^{(e)} = 1 + a_e$, $c_S^{(e)} = 1 + 2a_e$ for an electron [37], and $c_F^{(N)} = Z + a_N$, $c_S^{(N)} = Z + 2a_N$ for a spin 1/2 nucleon of charge Z [41], where a_e (resp. a_N) is the anomalous magnetic moment of the electron (resp. nucleus).

a factor 2-3 would allow an independent cross-check of the values of the Rydberg constant and nuclear radii [15].

The highest precision reached in experiments so far is $3.8 \cdot 10^{-10}$ on the fundamental rotational transition in HD^+ [13]. In this case, a single hyperfine component was measured, and comparison with theory is limited by hyperfine structure calculations [13,47]. Calculation of $m\alpha^6(m/M)$ order corrections to the spin-orbit and spin-spin tensor interactions in the three-body framework is currently in progress to improve this, following previous work on the spin-spin contact Fermi interaction [48]. Spin-averaged interaction potentials at the same order have been recently derived [49].

Regarding spin-averaged transition frequencies, the largest source of theoretical uncertainty is the one-loop self-energy contribution at the $m\alpha^8$ order [35] which has not been calculated yet even in hydrogenlike systems. One possible way forward would be to calculate the one-loop self-energy of a bound electron in a two-center potential, without performing the expansion in powers of the binding potential, as previously done in hydrogenlike atoms [50,51].

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