High accuracy results for the energy levels of the molecular ions $H_2^+$, $D_2^+$ and $HD^+$, up to $J = 2$

J Ph Karr$^{1,2}$ and L Hilico$^{1,2}$

1 Département de Physique et Modélisation, Université d’Evry Val d’Essonne Boulevard F. Mitterrand, 91025 Evry cedex, France
2 Laboratoire Kastler Brossel, Université Pierre et Marie Curie T12, Case 74, 4 Place Jussieu, 75252 Paris, France

E-mail: karr@spectro.jussieu.fr

Received 20 February 2006, in final form 15 March 2006
Published 10 April 2006
Online at stacks.iop.org/JPhysB/39/2095

Abstract

We present a nonrelativistic calculation of the rotation-vibration levels of the molecular ions $H_2^+$, $D_2^+$ and $HD^+$, relying on the diagonalization of the exact three-body Hamiltonian in a variational basis. The $J = 2$ levels are obtained with a very high accuracy of $10^{-14}$ au (for most levels) representing an improvement by five orders of magnitude over previous calculations. The accuracy is also improved for the $J = 1$ levels of $H_2^+$ and $D_2^+$ with respect to earlier works. Moreover, we have computed the sensitivities of the energy levels with respect to the mass ratios, allowing these levels to be used for metrological purposes.

1. Introduction

In recent years, precise calculations in the hydrogen molecular ion $H_2^+$ and its isotopes have attracted interest, because these systems appear as promising candidates for the metrology of the electron to proton mass ratio $M_e/M_p$, or the ratios of the nuclear masses $M_D/M_P$ [1–3]. Almost all the rotation-vibration levels of $HD^+$, $H_2^+$ and $D_2^+$ including relativistic and radiative corrections have been computed by Moss [4–6] with an accuracy of $10^{-9}$ au. Recent progress in variational calculations has allowed to improve the accuracy of the nonrelativistic calculations up to $10^{-14}$ or even $10^{-18}$ for the lowest levels [1, 2, 7–9], while the accuracy on relativistic and QED corrections is also improving and should reach $10^{-10}$–$10^{-11}$ au [10, 11]. However, the optical transitions that may be used in metrology experiments also involve more excited states [1, 2] especially in the perspective of comparing several transition frequencies to test the time independence of the mass ratios as proposed in [3]. It would then be useful to extend the high-precision calculations as far as possible into the rotation-vibration spectrum.

To our knowledge, our method relying on the use of perimetric coordinates is the only one that allows to maintain a high accuracy up to the most excited vibrational states with...
reasonable numerical means \cite{1,2}. Indeed, this set of coordinates takes advantage of the dynamical symmetries of the three-body Coulomb problem, so that it is possible to choose a basis in which the Hamiltonian has strict coupling rules, and whose wavefunctions have the correct long-range behaviour. However, as was already discussed in \cite{1}, this method becomes less and less advantageous when the value of $J$ increases; only the $J=0$ and $J=1$ states have been computed so far, with an accuracy of $10^{-14}$ au for all levels except for the last excited state and the $J=1$ states of $\mathrm{H}_2^+$ and $\mathrm{D}_2^+$ due to a higher numerical instability. In this paper, we extend our method to the $J=2$ states and show that it remains advantageous with respect to the usual methods relying on Hylleraas coordinates. For convenience, we have regrouped all our results in the present paper; all levels have been recomputed with the values of the most recent (2002) CODATA \cite{12}, and we also give their sensitivity with respect to the mass ratios. The accuracy for the $J=1$ states of $\mathrm{H}_2^+$ and $\mathrm{D}_2^+$ has been improved to $10^{-14}$ au.

In the first section, we briefly recall the main features of our method (more details can be found in \cite{1}). The second section is devoted to the presentation of numerical results.

2. Method of resolution

2.1. Hamiltonian

Using centred Jacobi coordinates, the Hamiltonian of a three-body molecular ion with nuclear masses $M_1$ and $M_2$ can be written as

$$H = \frac{q^2}{4\pi \varepsilon_0 a_0} \left( \frac{p_r^2}{2} + \frac{1}{2\mu_{12}} \left( \frac{1}{\mu_0} - \frac{1}{\mu_0/2 - r} - \frac{1}{\mu_0/2 + r} + \frac{1}{R} \right) \right),$$

where $q$ is the electron charge, $a_0$ is the atomic Bohr radius, $\mu_{12} = M_1 M_2/m_e(M_1 + M_2)$ is the reduced mass of the two nuclei in units of $m_e$ and $1/\mu_0 = m_e(1/M_1 - 1/M_2)$. The dimensionless quantities $R$ and $r$ represent respectively the relative position of the two nuclei and the position of the electron with respect to their centre of mass. The quantities $P$ and $p$ are the conjugate momenta. The term in $p.P$ is the so-called symmetry breaking term, which vanishes for the homonuclear ions $\mathrm{H}_2^+$ and $\mathrm{D}_2^+$.

2.2. Structure of the wavefunctions

The rotational invariance yields the following separation between angular and radial variables:

$$\Psi^{JM}(R, r) = \sum_{T=-J}^{J} D^{JM}_{M'T}(\psi, \theta, \phi) \Phi^{JM}_{T}(R, \rho, \zeta),$$

where the radial coordinates $R$, $\rho$, $\zeta$ have been defined in \cite{1}, $\psi, \theta, \phi$ are the Euler angles, and $D^{JM}_{M'T}$ are known angular functions related to the matrix elements of the rotation operator. As a result, for a given value of $J$ and $M$, the wavefunctions are represented by $2J + 1$ unknown radial functions.

Another symmetry of the Hamiltonian is the parity $\Pi$. Since the parity only affects the angular part of the wavefunction, it is useful to introduce even and odd angular functions; from the $2J + 1$ functions $D^{JM}_{M'T}$ one obtains $J$ functions of parity $\Pi = (-1)^{J+1}$ and $J + 1$ functions of parity $\Pi = (-1)^J$.

In this paper, we consider bound states that are supported by the first Born–Oppenheimer curve (1s$\sigma_g$) with a total angular momentum $J \leq 2$. These states have the symmetries $S^o$, $P^o$,
High accuracy results for the energy levels of the molecular ions $\text{H}_2^+$, $\text{D}_2^+$ and $\text{HD}^+$, up to $J = 2097$

Table 1. For all the computed levels, we have indicated in this table: the radial functions representing the wavefunction, and (if necessary) their symmetry with respect to the exchange of $y$ and $z$; the basis size as a function of $N_{\text{tot}}$, where $N_{\text{tot}}$ is the number of Sturmian functions $|n_x, n_y, n_z\rangle$ verifying $n_x + n_y + n_z \leq N$ and $n_x \leq N_x$; the coupling rules between $|n_x, n_y, n_z\rangle$ and $|n_x + \Delta n_x, n_y + \Delta n_y, n_z + \Delta n_z\rangle$ and the number of coupling rules. Finally, for a typical value of $N$ and $N_x$ we give the basis size and the width of the matrix.

| $J = 0$ | $J = 1$ | $J = 2$ |
|---------|---------|---------|
| Radial wavefunction | $\text{H}_2^+$, $\text{D}_2^+$, $\text{HD}^+$ | $\text{H}_2^+$, $\text{D}_2^+$, $\text{HD}^+$ | $\text{H}_2^+$, $\text{D}_2^+$, $\text{HD}^+$ |
| Basis size | $F = \tilde{F}$ | $F$ | $F$ |
| | $2N_{\text{tot}}$ | $2N_{\text{tot}}$ | $2N_{\text{tot}}$ |
| | $|\Delta n_{x,y,z}| \leq 2$, | $|\Delta n_{x,y,z}| \leq 4$, | $|\Delta n_{x,y,z}| \leq 6$, |
| | $|\Delta n_x| + |\Delta n_y| + |\Delta n_z| \leq 3$ | $|\Delta n_x| + |\Delta n_y| + |\Delta n_z| \leq 5$ | $|\Delta n_x| + |\Delta n_y| + |\Delta n_z| \leq 7$ |
| Number of coupling rules | 57 | 450 | 1707 |
| Basis size | 11 964 | 23 496 | 23 496 |
| Width | 834 | 1364 | 3031 |

$D^c$ and the corresponding separation between angular and radial variables is written, in the case of $M = 0$ states:

$S^c$ states: $\Psi^{00}(R, r) = \Phi^0(R, \rho, \zeta)$

$P^c$ states: $\Psi^{10}(R, r) = D_{00}^1(\psi, \theta, \phi) \Phi^0(R, \rho, \zeta)$

As a result, the radial part of the wavefunction is represented by $J + 1$ radial functions $\Phi^i(R, \rho, \zeta)$.

2.3. Factorization of the radial part

The separation introduced in the previous section allows us to write down an effective Schrödinger equation for the radial part of the wavefunctions (for $J > 0$ it is in fact a system of coupled equations involving the $J + 1$ radial functions $\Phi^i(R, \rho, \zeta)$). In order to
Table 2. Energies of the $^1S^e$, $^3P^o$ and $^1D^e$ bound levels of the H$_2^+$ molecular ion below the first dissociation limit, in atomic units. The star indicates that there is no bound level.

| ν/J | 0 | 1 | 2 |
|-----|---|---|---|
| 0   | −0.597 139 063 079 39 | −0.596 873 738 784 71 | −0.596 345 205 489 39 |
| 1   | −0.587 155 679 096 19 | −0.586 904 320 919 19 | −0.586 403 631 528 69 |
| 2   | −0.577 751 904 415 08 | −0.577 514 034 057 45 | −0.577 040 237 163 02 |
| 3   | −0.568 098 498 730 86 | −0.568 683 708 260 19 | −0.568 235 992 971 58 |
| 4   | −0.559 609 220 849 67 | −0.559 397 171 550 16 | −0.559 032 389 906 00 |
| 5   | −0.551 300 749 896 55 | −0.551 045 393 957 06 | −0.550 534 935 971 07 |
| 6   | −0.543 458 999 278 75 | −0.543 193 708 260 19 | −0.542 754 392 906 00 |
| 7   | −0.536 142 722 733 45 | −0.535 780 673 62 | −0.535 396 806 281 70 |
| 8   | −0.529 086 284 367 52 | −0.528 722 733 45 | −0.528 333 500 606 38 |
| 9   | −0.522 650 992 971 58 | −0.522 296 389 906 00 | −0.522 142 722 733 45 |
| 10  | −0.516 874 174 628 27 | −0.516 519 814 659 29 | −0.516 268 806 281 70 |
| 11  | −0.511 000 365 278 75 | −0.510 641 393 957 06 | −0.510 396 806 281 70 |
| 12  | −0.505 396 806 281 70 | −0.505 142 722 733 45 | −0.504 780 673 62 |
| 13  | −0.500 142 722 733 45 | −0.500 032 389 906 00 | −0.500 887 754 205 98 |
| 14  | −0.495 032 389 906 00 | −0.495 780 673 62 | −0.495 534 935 971 07 |
| 15  | −0.490 492 303 036 23 | −0.490 238 846 906 00 | −0.490 032 389 906 00 |
| 16  | −0.486 155 679 096 19 | −0.486 032 389 906 00 | −0.486 887 754 205 98 |
| 17  | −0.482 754 392 906 00 | −0.482 534 935 971 07 | −0.482 333 500 606 38 |
| 18  | −0.479 722 733 45 | −0.479 534 935 971 07 | −0.479 333 500 606 38 |
| 19  | −0.477 839 712 26 au | * | *

* result taken from [5]. The first dissociation limit of H$_2^+$ is $-1/2(1 + m_e/M_p)^{-1} = -0.499 727 839 712 26$ au.

Using these expressions, we can write down a set of effective Schrödinger equations for the radial functions $F, G, H$ appearing in (6)–(7), in which centrifugal terms of the type $1/R^2$ have disappeared. The effective Hamiltonian $H_{\text{eff}}$ appearing in these equations can be found in [1] for $P^o$ states.
2.4. Exchange symmetry

In the cases of \( \text{H}_2^+ \) and \( \text{D}_2^+ \), we have an additional symmetry corresponding to the exchange of the two nuclei. The wavefunctions are either symmetric or antisymmetric with respect to the exchange operator \( P_{12} \). Like in the atomic case, we will note here spatially symmetric (respectively antisymmetric) as singlets (respectively triplets). The bound states of \( \text{H}_2^+ \) and \( \text{D}_2^+ \) that are considered in this paper have the following symmetries: \( 1\,S^e, \, 3\,P^o \) and \( 1\,D^e \).

The effect of the exchange operator on radial functions is the transformation \( \zeta \longrightarrow -\zeta \). Thus the radial functions of singlet and triplet states differ by their behaviour, either symmetric or antisymmetric under the transformation \( \zeta \longrightarrow -\zeta \). For the states considered here, the radial functions have the following properties:

\begin{align*}
1\,S^e \text{ states:} & \quad F = \tilde{F} \\
3\,P^o \text{ states:} & \quad G = -\tilde{F} \\
1\,D^e \text{ states:} & \quad G = \tilde{F} \quad \text{and} \quad H = \tilde{H},
\end{align*}

where \( \tilde{F}(R, \rho, \zeta) = F(R, \rho, -\zeta) \).

2.5. Numerical implementation

Even though the centrifugal terms have been eliminated, divergences in \( 1/r_1, 1/r_2 \) and \( 1/R \) remain due to the Coulomb potential \( (r_{1(2)} = \|R \pm r/2\| \) are the distances between the electron and the two nuclei). These divergences can be regularized through multiplication of
the Schrödinger equation by $r_1 r_2 R$. The Schrödinger equation is turned into a generalized eigenvalue problem, which is written as

$$A |\Psi\rangle = E B |\Psi\rangle$$

with $B = r_1 r_2 R$ and $A = B H_{\text{eff}}$.

Our numerical method to solve this problem has been explained in detail in [1]. It relies on the use of perimetric radial coordinates, defined by

$$x = r_1 + r_2 - R$$
$$y = r_1 - r_2 + R$$
$$z = -r_1 + r_2 + R,$$

and Sturmian basis functions in the $x, y, z$ coordinates

$$|n^x, n^y, n^z\rangle = |n^x\rangle \otimes |n^y\rangle \otimes |n^z\rangle,$$

where $|n^x\rangle$ represents the function

$$\Phi_n(au) = (u|n^x\rangle = (-1)^n \sqrt{a} L_n^{(0)}(au) e^{-au^2/2}.$$  

$n$ is a non-negative integer and $L_n^{(0)}$ are the generalized Laguerre polynomials. $a^{-1}$ is a length scale in the $x$ direction, $\beta^{-1}$ in the $y$ and $z$ directions.

| $v/J$ | 0 | 1 | 2 |
|-------|---|---|---|
| 0     | $-0.598 788 784 304 46$ | $-0.598 654 873 192 49$ | $-0.598 387 585 778 48$ |
| 1     | $-0.591 603 121 831 23$ | $-0.591 474 211 454 95$ | $-0.591 216 909 547 45$ |
| 2     | $-0.584 712 206 896 08$ | $-0.584 588 169 503 36$ | $-0.584 340 598 262 38$ |
| 3     | $-0.578 108 591 284 75$ | $-0.577 989 311 807 81$ | $-0.577 751 241 739 67$ |
| 4     | $-0.571 785 998 461 03$ | $-0.571 670 974 249 74$ | $-0.571 442 200 677 76$ |
| 5     | $-0.565 737 302 734 64$ | $-0.565 627 243 389 04$ | $-0.565 407 586 123 15$ |
| 6     | $-0.559 958 513 978 72$ | $-0.559 852 941 284 34$ | $-0.559 642 244 496 68$ |
| 7     | $-0.554 444 767 877 07$ | $-0.554 343 615 849 03$ | $-0.554 141 748 167 64$ |
| 8     | $-0.549 192 321 773 66$ | $-0.549 095 538 818 38$ | $-0.548 902 391 656 91$ |
| 9     | $-0.544 198 156 295 12$ | $-0.544 105 697 502 03$ | $-0.543 921 193 650 73$ |

* result taken from [6]. The first dissociation limit of $D^+_2$ is $-0.499 863 815 247 21$ au.
High accuracy results for the energy levels of the molecular ions $H_2^+$, $D_2^+$ and $HD^+$, up to $J = 2$

**Table 5.** Derivatives $10^3 \lambda \partial E / \partial \lambda$ of the energies of $D_2^+$ with respect to the electron/deuteron mass ratio $\lambda$ (in atomic units). The hyphens correspond to levels for which the accuracy of the calculation is not sufficient to be sensitive to a change of the recommended value of the deuteron/electron mass ratio.

| $v/J$ | 0      | 1      | 2      |
|-------|--------|--------|--------|
| 0     | 0.197274 | 0.210525 | 0.236919 |
| 1     | 0.541450 | 0.553958 | 0.578871 |
| 2     | 0.856748 | 0.868537 | 0.892017 |
| 3     | 1.14421  | 1.15530  | 1.17739  |
| 4     | 1.40471  | 1.41513  | 1.43586  |
| 5     | 1.63901  | 1.64876  | 1.66817  |
| 6     | 1.84769  | 1.85679  | 1.87490  |
| 7     | 2.03120  | 2.03966  | 2.05649  |
| 8     | 2.18987  | 2.19769  | 2.21325  |
| 9     | 2.32384  | 2.33103  | 2.34533  |
| 10    | 2.43313  | 2.43968  | 2.45272  |
| 11    | 2.51759  | 2.52351  | 2.53527  |
| 12    | 2.57682  | 2.58219  | 2.59266  |
| 13    | 2.61062  | 2.61523  | 2.62438  |
| 14    | 2.61801  | 2.62194  | 2.62973  |
| 15    | 2.59819  | 2.60142  | 2.60780  |
| 16    | 2.55004  | 2.55253  | 2.55744  |
| 17    | 2.47217  | 2.47388  | 2.47724  |
| 18    | 2.36289  | 2.36378  | 2.36549  |
| 19    | 2.22021  | 2.22071  | 2.22013  |
| 20    | 2.04174  | 2.04077  | 2.03874  |
| 21    | 1.82476  | 1.82270  | 1.81852  |
| 22    | 1.56020  | 1.56293  | 1.55630  |
| 23    | 1.26306  | 1.25840  | 1.24896  |
| 24    | 0.913898 | 0.907605 | 0.894869 |
| 25    | 0.526414 | 0.518342 | –        |
| 26    | 0.168515 | –        | –        |
| 27    | 0.033736 | –        | –        |

For $H_2^+$ and $D_2^+$, due to the exchange symmetry, some of the radial wavefunctions can be either symmetric or antisymmetric with respect to the transformation $\zeta \rightarrow -\zeta$, that is the exchange of $y$ and $z$. In such cases we use a symmetrized or antisymmetrized basis:

$$|n_x, n_y, n_z\rangle^\pm = \frac{|n_x, n_y, n_z\rangle \pm |n_x, n_z, n_y\rangle}{\sqrt{2}}. \quad (15)$$

To perform the numerical calculations, the basis is truncated at $n_x + n_y + n_z \leq N$ and $n_x \leq N_x$, with $N_x \leq N$. If the basis is symmetrized (respectively, antisymmetrized) we add the condition $n_x \leq n_z$ (respectively, $n_y < n_z$) which reduces the size of the basis by a factor of about 2. Since the radial part of the wavefunction is represented by $J + 1$ radial functions, the size of the matrices representing the $A$ and $B$ operators also depends on $J$. The different cases are summarized in table 1.

Because of their structure, all the terms in the Hamiltonian have strict coupling rules. $A$ and $B$ are then sparse band matrices having exactly the same shape; the order of the basis vectors is chosen in order to minimize their width around the diagonal. The coupling rules and width are also reported in table 1; the fact that the number of coupling rules increases with
Table 6. Energies of the $S^\prime$, $P^\prime$ and $D^\prime$ bound levels of the HD$^+$ molecular ion. The star indicates that there is no bound level.

| $v/J$ | 0          | 1          | 2          |
|-------|------------|------------|------------|
| 0     | $-0.597979$ | $0.686093$ | $0.0921$   |
| 1     | $-0.381818$ | $0.55696$  | $0.0921$   |
| 2     | $-0.589037$ | $0.21837$  | $0.0921$   |
| 3     | $-0.570546$ | $0.55187$  | $0.0921$   |
| 4     | $-0.566112$ | $0.042078$ | $0.0921$   |
| 5     | $-0.555752$ | $0.82556$  | $0.0921$   |
| 6     | $-0.551935$ | $0.49586$  | $0.0921$   |
| 7     | $-0.546859$ | $0.15292$  | $0.0921$   |
| 8     | $-0.538206$ | $0.64154$  | $0.0921$   |
| 9     | $-0.534337$ | $0.013561$ | $0.0921$   |
| 10    | $-0.522336$ | $0.635566$ | $0.0921$   |
| 11    | $-0.524510$ | $0.910171$ | $0.0921$   |
| 12    | $-0.520147$ | $0.77622$  | $0.0921$   |
| 13    | $-0.516218$ | $0.709961$ | $0.0921$   |
| 14    | $-0.512602$ | $0.192252$ | $0.0921$   |
| 15    | $-0.509004$ | $0.651335$ | $0.0921$   |
| 16    | $-0.506763$ | $0.851737$ | $0.0921$   |
| 17    | $-0.504452$ | $0.699457$ | $0.0921$   |
| 18    | $-0.502589$ | $0.233892$ | $0.0921$   |
| 19    | $-0.501000$ | $0.799118$ | $0.0921$   |
| 20    | $-0.500000$ | $0.245420$ | $0.0921$   |
| 21    | $-0.499900$ | $0.361470$ | $0.0921$   |
| 22    | $-0.499865$ | $0.7785$   | $0.0921$   |

* result taken from [4]. The two dissociation limits of HD$^+$ are HD$^+ \rightarrow$ D+H$^+$ (given in the caption of table 4) and HD$^+ \rightarrow$ H+D$^+$ (given in the caption of table 2).

$J$ is due to the factorization, which involves polynomials of degree $J$ (see equation (6)-(7)). As a result, with increasing $J$ the matrices become both larger and wider.

The analytical calculation of the matrix elements of the various contributions to the Hamiltonian has been performed using the symbolic calculation language Mathematica 4. The results are directly output in the double precision FORTRAN code. The generalized eigenvalue problem is then diagonalized using the Lanczos algorithm. That gives the eigenvectors and eigenvalues in the energy range of interest.

### 3. Numerical results

The energy levels of H$_2^+$, D$_2^+$ and HD$^+$ are given in tables 2, 4 and 6. The mass ratios are taken from the 2002 CODATA [12]: $M_p/m_e = 1836.1527261$ and $M_D/m_e = 3670.4829652$. The atomic unit of energy is 219474.6313705 cm$^{-1}$. All the digits shown in these tables are converged; an accuracy of $10^{-14}$ au, limited by the numerical noise, is achieved for most levels. Let us stress that these results were obtained with quite reasonable computation resources, i.e. a single standard workstation with 8 Go memory and double precision arithmetic.

When the accuracy is sufficient to be sensitive to the mass ratios, we have computed the normalized sensitivity $\lambda \partial E/\partial \lambda$ of the energy levels to the variation of the relevant mass ratio(s), that is the electron/nucleus mass ratio $\lambda = m_e/M_p$ for H$_2^+$ or HD$^+$ ($\lambda = m_e/M_D$ for D$_2^+$) and the ratio of the nuclear masses $\mu = M_p/M_D$ for HD$^+$, following the method...
High accuracy results for the energy levels of the molecular ions H$_2^+$, D$_2^+$ and HD$^+$, up to $J = 2$.

Table 7. Derivatives of the energies of HD$^+$ with respect to the electron/proton and proton/deuteron mass ratios, respectively noted $\lambda$ and $\mu$ (in atomic units). The hyphens correspond to levels for which the accuracy of the calculation is not sufficient to be sensitive to a change of the recommended value of the mass ratios.

| $\nu/J$ | 0     | 1     | 2     |
|---------|-------|-------|-------|
|         | $10^2\lambda\partial E/\partial \lambda$ | $10^2\mu\partial E/\partial \mu$ | $10^2\lambda\partial E/\partial \lambda$ | $10^2\mu\partial E/\partial \mu$ |
| 0       | 0.244 262 | 0.083 468 | 0.263 983 | 0.088 045 | 0.303 187 | 0.101 120 |
| 1       | 0.657 496 | 0.219 284 | 0.675 865 | 0.225 410 | 0.712 375 | 0.237 586 |
| 2       | 1.027 99  | 0.342 846 | 1.045 06  | 0.348 538 | 1.078 98  | 0.359 851 |
| 3       | 1.357 53  | 0.452 749 | 1.373 34  | 0.458 023 | 1.404 76  | 0.468 501 |
| 4       | 1.647 56  | 0.549 475 | 1.662 15  | 0.554 342 | 1.691 14  | 0.564 011 |
| 5       | 1.899 20  | 0.633 398 | 1.912 60  | 0.637 864 | 1.939 22  | 0.646 744 |
| 6       | 2.113 25  | 0.704 785 | 2.125 48  | 0.708 864 | 2.149 37  | 0.724 808 |
| 7       | 2.290 18  | 0.763 794 | 2.301 25  | 0.767 485 | 2.323 21  | 0.774 808 |
| 8       | 2.430 14  | 0.810 472 | 2.440 04  | 0.813 775 | 2.459 68  | 0.820 325 |
| 9       | 2.532 91  | 0.844 748 | 2.541 65  | 0.847 661 | 2.558 95  | 0.853 431 |
| 10      | 2.597 93  | 0.866 431 | 2.605 46  | 0.868 946 | 2.620 39  | 0.873 922 |
| 11      | 2.624 19  | 0.875 192 | 2.630 50  | 0.877 298 | 2.642 97  | 0.881 457 |
| 12      | 2.610 27  | 0.870 553 | 2.615 31  | 0.872 233 | 2.625 23  | 0.875 541 |
| 13      | 2.554 23  | 0.851 869 | 2.557 92  | 0.853 100 | 2.565 16  | 0.855 512 |
| 14      | 2.453 57  | 0.818 302 | 2.455 82  | 0.819 055 | 2.460 18  | 0.820 508 |
| 15      | 2.305 10  | 0.768 797 | 2.305 80  | 0.769 029 | 2.307 03  | 0.769 442 |
| 16      | 2.104 90  | 0.702 043 | 2.103 87  | 0.701 702 | 2.101 66  | 0.700 964 |
| 17      | 1.848 18  | 0.616 454 | 1.845 22  | 0.615 466 | 1.839 11  | 0.613 429 |
| 18      | 1.529 38  | 0.510 190 | 1.524 17  | 0.508 453 | 1.513 52  | 0.504 907 |
| 19      | 1.142 72  | 0.381 394 | 1.134 80  | 0.378 759 | 1.119 25  | 0.372 827 |
| 20      | 0.684 174 | 0.229 190 | 0.672 638 | 0.225 385 | –         | –         |
| 21      | 0.142 706 | 0.054 888 | 0.128 607 | 0.050 433 | –         | –         |
| 22      | –         | –         | –         | –         | *         | *         |

The precision for the $J = 1$ states of H$_2^+$ and D$_2^+$ has been improved from $10^{-11}$ to $10^{-14}$ au with respect to earlier results [1]. As discussed in [1], the increased numerical noise was due to round off errors that accumulate more rapidly during the Lanczos steps, because the matrices are ill-conditioned. However, for a given eigenvalue $E_n$ the accuracy of the result can be improved by solving the problem $(A - \lambda B)|\Psi\rangle = E|\Psi\rangle$ with $\lambda$ close to $E_n$. In this way, the eigenvalue is converged during the first few Lanczos steps and the round off errors are greatly reduced. Of course, the downside is that a new matrix has to be diagonalized for each level, which multiplies the computation time by the number of computed levels.

For $J = 2$ levels, the conditioning properties of the matrices are even worse than for $J = 1$ levels. It is not surprising that the conditioning should worsen when $J$ increases, because their matrix elements are polynomials in $n_x, n_y, n_z$, the degree of which increases with $J$ since the degree of the polynomials appearing in the factorization increases (see expressions (6), (7)). However, for most levels it is still possible to achieve an accuracy of $10^{-14}$ au. Only for the
last few levels (for example $v = 16$ and $v = 17$ in $\text{H}_2^+$, or $v = 20$ to 24 in $\text{D}_2^+$) does the numerical accuracy drop to $10^{-13}$, because of the increased basis size. On the whole, for most levels the precision has been improved by 4 or 5 orders of magnitude with respect to earlier works [4–6] except for the first vibrational levels of $\text{HD}^+$ ($v = 0$ to $v = 4$) which had been computed with $10^{-14}$ or $10^{-15}$ accuracy in [3]. We have checked that our results are in full agreement with those of that reference.

Finally, let us note that for $J = 0$ and $J = 1$, only the last vibrational level (or the last two levels) could not be converged to $10^{-14}$ accuracy due to the limit in memory size. $J = 2$ levels demand more memory (since the matrices are both larger and wider, see table 1) which is why the level of convergence drops for the last three or four vibrational levels. Whenever the accuracy of our calculations did not reach $10^{-9}$–$10^{-10}$ au we have reported the more precise results obtained by Moss [4–6]; although these results have been obtained with the 1986 CODATA values of the mass ratios, all the digits remain valid because the sensitivity of the last vibrational levels is very low.

All these elements make it clear that our method becomes less and less convenient when $J$ increases. It may be possible to extend the calculations to $J = 3$ states, but then two problems will occur:

- the limit in memory will prevent the calculation of a larger number of levels;
- conditioning problems will become more severe; unless an efficient method of pre-conditioning of the matrices can be devised, quadruple precision arithmetic is likely to be compulsory in this case which imposes new constraints in terms of memory and computation time.

4. Conclusion

We have shown that the use of perimetric coordinates allows us to obtain high accuracy results for the nonrelativistic rotation-vibration energies of the hydrogen molecular ion and its isotopes, up to $J = 2$; our results suggest that this is probably the last value of $J$ for which this method is advantageous with respect to usual methods relying on Hylleraas coordinates. The very accurate wavefunctions that we obtain enable the calculation of relativistic and radiative corrections with an improved precision, which is in progress. These results extend the range of optical transitions on which high-precision measurements can be compared to theoretical predictions for metrological applications.

Acknowledgments

The authors wish to thank D Delande and B Grémaud for fruitful discussions and also for providing us the Lanczos diagonalization code. Laboratoire Kastler Brossel de l’Université Pierre et Marie Curie et de l’Ecole Normale Supérieure is UMR 8552 du CNRS.

References

[1] Hilico L, Billy N, Grémaud B and Delande D 2000 Eur. Phys. J. D 12 449–66
[2] Karr J Ph, Kilic S and Hilico L 2005 J. Phys. B: At. Mol. Opt. Phys. 38 853–66
[3] Schiller S and Korobov V 2005 Phys. Rev. A 71 032505
[4] Moss R E 1993 Mol. Phys. 78 371
[5] Moss R E 1993 Mol. Phys. 80 1541
[6] Moss R E 1993 J. Chem. Soc. Faraday Trans. 89 3851
High accuracy results for the energy levels of the molecular ions \( \text{H}_2^+ \), \( \text{D}_2^+ \) and \( \text{HD}^+ \), up to \( J = 2 \)

[7] Korobov V I 2000 Phys. Rev. A 61 064503
[8] Bailey D H and Frolov A M 2002 J. Phys. B: At. Mol. Opt. Phys. 35 4287
[9] Yan Z C, Zhang J Y and Li Y 2003 Phys. Rev. A 67 062504
[10] Korobov V I 2004 Phys. Rev. A 70 012505
[11] Korobov V I 2006 Phys. Rev. A 73 024502
[12] http://physics.nist.gov/cuu/Constants/
[13] Schwartz C 1961 Phys. Rev. 123 1700