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A nonadiabatic lower bound calculation of H_2^+ and D_2^+

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Accurate nonadiabatic lower and upper bounds for groundstate energies of H_2^+ and D_2^+ are calculated with the linearized method of variance minimization. The results in a.u. are

$$-0.59713906_3 < E_0(H_2^+) < -0.59713899_4$$

$$-0.59878877_5 < E_0(D_2^+) < -0.59877873_8$$

i.e. the values are determined with an absolute error smaller than 0.02 cm^{-1} for H_2^+ and 0.01 cm^{-1} for D_2^+.

Key words: Eigenvalue problems

1. Introduction

The determination of accurate lower bounds for eigenvalues of Schrödinger operators is still a hard problem even for the simplest possible molecules, i.e. H_2^+ and D_2^+. We wish to show how the principle of variance minimization in connection with Temple's formula can be applied to this problem. Let H be a selfadjoint operator with a discrete spectrum $\sigma_d = \{E_i \mid E_0 < E_1 < \cdots\}$ below the bottom of the continuum and domain D_H. From Temple's formula

$$E_0 \geq (Hu \mid u) - \frac{\|Hu\|^2 - (Hu \mid u)^2}{\rho - (Hu \mid u)}, \qquad \|u\| = 1 \tag{1}$$

with $E_0 < \rho < E_1$ it can be seen [1] that a crucial point for the determination of a good lower bound is the minimization of the variance

$$F[u] = \|Hu\|^2 - (Hu \mid u)^2$$

As has been shown [2], [3] this aim can be achieved by applying the method of variance minimization.

2. The Hamiltonian and the basic functions

After separation of translational and rotational coordinates the Schrödinger operator for a homonuclear diatomic one-electron molecule in elliptical coordinates is [4]

$$H = H_0 + H'$$

$$H^0 = -\tfrac{1}{2}\Delta_e - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

$$H' = -\frac{1}{2\mu}\Delta_R - \frac{1}{8\mu}\Delta_e$$

with

$$\Delta_R = \frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R} - \frac{2}{R^2} - \frac{2}{R^2}\frac{1}{\xi^2-\eta^2}X\left(1+R\frac{\partial}{\partial R}\right) + \frac{1}{R^2}\frac{\xi^2+\eta^2-1}{\xi^2-\eta^2}Y \tag{2}$$

$$\Delta_e = \frac{4}{R^2}\frac{1}{\xi^2-\eta^2}Y$$

$$\frac{1}{r_A} + \frac{1}{r_B} = \frac{4}{R}\frac{1}{\xi^2-\eta^2}$$

$$X = \xi(\xi^2-1)\frac{\partial}{\partial \xi} + \eta(1-\eta^2)\frac{\partial}{\partial \eta}$$

$$Y = \frac{\partial}{\partial \xi}\left[(\xi^2-1)\frac{\partial}{\partial \xi}\right] + \frac{\partial}{\partial \eta}\left[(1-\eta^2)\frac{\partial}{\partial \eta}\right].$$

For our calculation we choose the following basis set

$$v_i = e^{-a\xi}\xi^{\lambda_i}\eta^{\nu_i}\, e^{-\frac{1}{2}c^2(R-d)^2}H_{t_i}(c(R-d)) \tag{3}$$

with the real parameters a, c, d, exponents λ_i, ν_i and t_i being the order of the Hermite polynomial H_{t_i}. These basis functions differ from those, ϕ_i, used by Bishop [4] by omitting the factors cosh $b\eta$ and $R^{-3/2}$.

The first factor was omitted to make the integrals occurring in $\|Hv_i\|$ more convenient. However, the omission of the factor $R^{-3/2}$ is absolutely necessary because $H\phi_i \notin D_H$. Indeed the corresponding integral

$$\int_0^\infty R^{-2}\exp\left(-\tfrac{1}{2}c^2(R-d)^2\right)H_{t_i}(cR-d))\,dR$$

is divergent.

Applying the operator H, Eq. (2), on the basis functions v_i, i.e. Hv_i, yields a sum of $n = 38$ terms differing at least in one of the exponents (λ_i, v_i) or in the order t_i of the Hermite polynomial. Thus calculating $(Hv_i | Hv_j)$ we obtain $\frac{1}{2}n(n+1) = 741$ terms.

In order to handle this enormous number of terms a computer procedure was developed to calculate the product $(Hv_i | Hv_j)$ directly from basic integrals. Each of the 38 terms in Hv_i and Hv_j is determined one-to-one by a triplet (λ_p, ν_p, t_p) and (λ_q, ν_q, t_q) respectively. Therefore each of the terms in $(Hv_i | Hv_j)$ is determined one-to-one by the four numbers $(\lambda_p + \lambda_q, \nu_p + \nu_q, t_p, t_q)$. The integrals corresponding to these terms may be separated in a (ξ, η)-part characterized by $(\lambda_p + \lambda_q, \nu_p + \nu_q)$ and an R-part characterized by (t_p, t_q). These integrals are calculated and stored in advance. Concerning details of the procedure see [5].

3. Calculation of the eigenvalues

The determination of lower and upper bounds for the ground state of H_2^+ and D_2^+ respectively was done with the linearized method of variance minimization [3]. In order to apply Temple's formula (1) a good lower bound ρ for the first excited vibronic state is needed as well. Usually the lower bound of the first excited state obtained during the calculation for the groundstate is of sufficient accuracy. However, in this case the small difference between the energy levels demands an extra calculation of the lower bound of the first excited vibronic state. This was done by choosing suitable starting values close to E_1, E_2, E_3 respectively. In these cases the linearized method of variance minimization yields directly a lower bound for E_3 by $\lambda_3^* - \sqrt{F_3^*}$ [6] and thus more accurate lower bounds for E_2 and E_1 are obtained by successive application of Temple's formula. The best result was $\rho = 0.58722812$ a.u. Another crucial point is the optimization of the basis set. We systematically enlarged the basis set by raising the integers λ_i, ν_i, t_i in (3) with $\lambda_i = 0, 1, 2, 3, 4$; $\nu_i = 0, 2, 4, 6$ and $t_i = 0, 1, \ldots, 8$. We decided to use Bishop's parameters [4] $a = 1.6$, $c = 3.0$, $d = 2.1$ and later optimized these values for our basis using a set of 45 functions. We observed only a slight change in c with $c_{\text{opt}} = 3.8$. In order to avoid an unnecessary large basis we chose Bishop's method of selecting basis functions [5], finally obtaining a set of 300 functions. The results for H_2^+ are shown in Table 1 with

$$E_0 \leq E_0^* = \lambda_0^* - \frac{F_0^*}{\rho - \lambda_0^*}$$

and dim V_n the number of basis functions.

Table 1. Lower bounds E_0^* for the groundstate E_0 of H_2^+ in a.u.

dim V_n	$\lambda_i^{\max}$	$\nu_i^{\max}$	$t_i^{\max}$	F_0^*	λ_0^*	E_0^*
45	2	4	4	2.4933×10^{-5}	-0.596662350	-0.59930517_2
84	3	4	6	2.3568×10^{-6}	-0.597133585	-0.59737151_5
140	4	6	6	2.9846×10^{-7}	-0.597136370	-0.59716649_3
300	7	8	14	6.8912×10^{-10}	-0.597138994	-0.59713906_3

An analogue was obtained for D_2^+:

$$-0.59878877_5\ \text{a.u.} \leq E_0(D_2^+) \leq -0.59878873_8\ \text{a.u.}$$

As has been shown [7] accurate upper bounds are obtained simultaneously during the first step of the iteration. The upper and lower bounds noted in the abstract are taken from the calculations with dim $V_n = 300$.

Discussion

According to Herzberg and Jungen [8] the experimental dissociation energy of H_2^+ is $21\,379.8 \pm 0.4\ \text{cm}^{-1}$.

With our results and the theoretical dissociation limit [4] of H_2^+ at $109\,677.57\ \text{cm}^{-1}$ we get

$$21\,379.30\ \text{cm}^{-1} < E_{\text{diss}} < 21\,379.28\ \text{cm}^{-1}$$

which is in good agreement with the experimental result.

Taking account of the relativistic and radiative corrections of $0.11\ \text{cm}^{-1}$ [4], [9], [10] our theoretical value is within the limits of the experimental accuracy.

Appendix

In addition to the well known integrals from the calculation of $(H\psi|\psi)$ a new type of a singular integral occurs in $\|H\psi\|$, i.e.

$$I = \int_1^\infty \int_{-1}^1 \frac{e^{-\alpha\xi}\xi^u \eta^v}{\xi^2 - \eta^2}\, d\eta\, d\xi.$$

with

$$I = \int_1^2 \int_{-1}^1 \frac{e^{-\alpha\xi}\xi^u \eta^v}{\xi^2 - \eta^2}\, d\eta\, d\xi + \int_2^\infty \int_{-1}^1 \frac{e^{-\alpha\xi}\xi^u \eta^v}{\xi^2 - \eta^2}\, d\eta\, d\xi = I_2 + I_\infty$$

we obtain

$$I_2 = \int_1^2 e^{-\alpha\xi}\xi^{u+v-1} \ln\frac{\xi+1}{\xi-1}\, d\xi - 2 \sum_{i=1}^{v-1}{}' \frac{1}{i} \int_1^2 e^{-\alpha\xi}\xi^{u+v+1-i}\, d\xi$$

where the last summation $\sum'$ runs over odd i's and

$$I_\infty = \sum_{k=0}^{\infty} \int_2^\infty \int_{-1}^1 e^{-\alpha\xi}\xi^{u-2-2k}\eta^{v+2k}\, d\eta\, d\xi$$

$$= \sum_{k=0}^{\infty} \frac{2}{v+2k-1} \int_2^\infty e^{-\alpha\xi}\xi^{u-2-2k}\, d\xi$$

The retaining integrals over a single variable where solved numerically with the procedure CADRE [11]. All integrals where calculated to an accuracy of 20 digits.

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