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HIGH-ACCURACY UPPER AND LOWER BOUNDS FOR EIGENVALUES ILLUSTRATED WITH H_2^+†

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We have calculated, for the ground state of the hydrogen molecule ion H_2^+ at an internuclear distance of $R=2$ a.u., upper and lower bounds to the nonrelativistic Schrödinger energy E which differ in the eleventh significant figure. This calculation was carried out to illustrate a method which we are developing with the following advantages: Upper and lower bounds of comparable accuracy are obtained, and this accuracy may be carried as far as desired; no integrations of any kind are used; the algebra required and computer programming are elementary; no secular equations need be solved; excited states as well as ground states can be treated; and the wave equation need not be separable. In this method the wave function was expressed as an infinite series

$$\Psi = e^{-\delta\xi}(\xi+1)^{\gamma}\sum a_{kl}[(\xi-1)/(\xi+1)]^{k}(1-\eta^{2})^{l}$$

in which ξ and η are the usual confocal elliptic coordinates. Insertion of this expansion into the wave equation leads to the following recursion relation for the coefficients:

$$\begin{aligned}&[-2k(k-1)+2k(\gamma-2\delta-1)-4l^2-2l+\gamma(1+2\delta)]a_{k,l}\\&\quad+(k+1)^2a_{k+1,l}+[\gamma^2-2(k-1)\gamma\\&\quad+(k-1)^2]a_{k-1,l}+4(l+1)^2a_{k,l+1}\\&\quad+\alpha a_{k,l-1}=0,\end{aligned}$$

where $\delta=(-\frac{1}{2}R^2E)^{1/2}$, $\alpha=\frac{1}{2}R^2E$, and $\gamma=R/\delta-1$. Asymptotically, we expect the lowest eigenfunction at a large distance to approach spherical symmetry and to die off exponentially in the variable ξ. If the wrong value of the energy is inserted in the recursion relations and the above limiting spherical symmetry is imposed, we know that the solution will go to either plus or minus infinity at infinite radius depending upon whether E is larger than or smaller than a nearby eigenvalue. We impose this limiting spherical symmetry by truncating the equations at some order N (say, $N=10$), where we have set the coefficients $a_{k,l}$ to zero for $k+l=N$, except for a_{N0}. With this truncation the recursion formula gives a set of simultaneous equations which can be solved for a_{N0}, and for all the coefficients of order less than N, in terms of $a_{00}=1$. To solve the simultaneous equations, we used an efficient procedure based on their special form. The solutions of these simultaneous equations will change as we change N. From their sign, their size, and the way in which they change by increasing the order of truncation, one can judge whether the value of E used in the computation is less than or greater than the true eigenvalue.

Wind[1] gives the ground-state energy as −1.102 634 2 a.u. at this interatomic distance. Table I shows that for N large enough and the energy too low, the coefficients all increase or stay constant as the order of truncation in-

TABLE I. a_{r0}'s Computed for Various Orders of Truncation.

Index r	N=16	N=15	N=14	N=13
E = -1.1026342145				
1	.1678 10^{-1}	.1678 10^{-1}	.1678 10^{-1}	.1678 10^{-1}
2	.4039 10^{-3}	.4039 10^{-3}	.4039 10^{-3}	.4039 10^{-3}
3	.3514 10^{-4}	.3514 10^{-4}	.3514 10^{-4}	.3514 10^{-4}
4	.5147 10^{-5}	.5147 10^{-5}	.5147 10^{-5}	.5147 10^{-5}
5	.1017 10^{-5}	.1017 10^{-5}	.1017 10^{-5}	.1017 10^{-5}
6	.2453 10^{-6}	.2453 10^{-6}	.2453 10^{-6}	.2453 10^{-6}
7	.6888 10^{-7}	.6888 10^{-7}	.6888 10^{-7}	.6886 10^{-7}
8	.2251 10^{-7}	.2251 10^{-7}	.2250 10^{-7}	.2246 10^{-7}
9	.9581 10^{-8}	.9571 10^{-7}	.9557 10^{-7}	.9486 10^{-7}
10	.6835 10^{-8}	.6815 10^{-8}	.6790 10^{-8}	.6659 10^{-8}
11	.8291 10^{-8}	.8255 10^{-8}	.8210 10^{-8}	.7974 10^{-8}
12	.1278 10^{-7}	.1271 10^{-7}	.1263 10^{-7}	.1221 10^{-7}
13	.2086 10^{-7}	.2075 10^{-7}	.2061 10^{-7}	
14	.3425 10^{-7}	.3406 10^{-7}	.3383 10^{-7}	
15	.5580 10^{-7}	.5549 10^{-7}		
16	.8999 10^{-7}			
E = -1.1026342144				
1	.1678 10^{-1}	.1678 10^{-1}	.1678 10^{-1}	.1678 10^{-1}
2	.4039 10^{-3}	.4039 10^{-3}	.4039 10^{-3}	.4039 10^{-3}
3	.3514 10^{-4}	.3514 10^{-4}	.3514 10^{-4}	.3514 10^{-4}
4	.5145 10^{-5}	.5145 10^{-5}	.5145 10^{-5}	.5145 10^{-5}
5	.1013 10^{-5}	.1013 10^{-5}	.1013 10^{-5}	.1013 10^{-5}
6	.2374 10^{-6}	.2374 10^{-6}	.2374 10^{-6}	.2375 10^{-6}
7	.5421 10^{-7}	.5427 10^{-7}	.5433 10^{-7}	.5440 10^{-7}
8	-.4208 10^{-8}	-.4104 10^{-8}	-.3987 10^{-8}	-.3856 10^{-8}
9	-.3812 10^{-7}	-.3792 10^{-7}	-.3770 10^{-7}	-.3745 10^{-7}
10	-.7677 10^{-7}	-.7641 10^{-7}	-.7601 10^{-7}	-.7556 10^{-7}
11	-.1358 10^{-6}	-.1352 10^{-6}	-.1345 10^{-6}	-.1336 10^{-6}
12	-.2318 10^{-6}	-.2307 10^{-6}	-.2294 10^{-6}	-.2280 10^{-6}
13	-.3885 10^{-6}	-.3866 10^{-6}	-.3844 10^{-6}	-.3819 10^{-6}
14	-.6419 10^{-6}	-.6387 10^{-6}	-.6349 10^{-6}	
15	-.1048 10^{-5}	-.1042 10^{-5}		
16	-.1691 10^{-5}			

creases. They first decrease and then increase as the index r increases for a given order of truncation. Consequently, as the order of truncation is extended to infinity, we see that the solution of the differential equation would ultimately go to $+\infty$ for $\eta = 0$ and $\xi \rightarrow \infty$. Similarly for an energy too high, the coefficients eventually all become algebraically smaller or stay constant as the order of truncation is increased, and first diminish in absolute value and then increase in absolute value as the index is increased. Consequently, as the order of truncation is extended to infinity, the solution goes to $-\infty$ for $\eta = 0$ and $\xi \rightarrow \infty$. This behavior of the solution shows that we have bracketed the true eigenvalue. Greater accuracy could be obtained if needed by subdividing the grid for E and repeating the calculation. The result agrees with Wind's value to the accuracy he claimed. In addition to the eigenvalue, this method provides a rapidly convergent expansion for the eigenfunction and hence the capability of providing expectation values of known accuracy. Less than a minute and a half of IBM-7094 time was required.

We have also tried this method on a number of simple one-dimensional problems, where it works extremely efficiently to give rigorous upper and lower bounds of almost any desired accuracy, and we are exploring its possibilities for application to more involved problems.

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SPIN-ORBIT COUPLING PARAMETER FOR Mn^{2+} IN $RbMnF_3$

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Fine structure observed in the ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$ band in the absorption spectrum of $RbMnF_3$ at 77°K has been assigned to the spin-orbit splitting of the ${}^4T_{2g}(D)$ level, and the analysis yields a value of 320 ± 10 cm^{-1} for the parameter ξ_{3d}.

The experimental value of the spin-orbit coupling parameter ξ for Mn^{2+} having d^5 configuration is known neither for the free ion nor for any crystal. In the case of the free ion, the spin-orbit splitting is of second order (half-filled shell), and it is not possible to obtain a reliable value of ξ by a least-squares fit to the spectrum of free Mn^{2+} ion. Manganous salts that have usually been studied have a lower than cubic symmetry, and because of the uncertainties in finding the contribution from the lower symmetry components of the crystalline field, it has not been possible to obtain the value of ξ from the fine structure observed in the absorption bands.[1] In order to avoid this difficulty, $RbMnF_3$ crystal, which has a cubic structure,[2] was chosen for the present study.

The absorption band having ${}^4T_{2g}(D)$ as upper state is found to be particularly suitable since the spin-orbit splitting of ${}^4T_{2g}(D)$ level is theoretically expected to be quite large.[3,4] Moreover, as this level has a small slope in the energy-level diagram, it is expected that these small splittings will be resolved in the spectra taken at low temperatures.

Under the spin-orbit interaction a ${}^4T_{2g}$ level splits as

$$T_{2g} \otimes \Gamma_8 = \Gamma_6 + \Gamma_7 + 2\Gamma_8.$$

First-order energies of the split levels using fictitious $L' = 1$ and $S = \frac{3}{2}$ are

$$E = 5a(\Gamma_7),\ 2a(\Gamma_8),\ \text{and}\ -3a(\Gamma_6 + \Gamma_{8'}),$$

where a is a proportionality constant.[3] The exact calculations of the spin-orbit splitting involve parameters B, C, Dq, α (Trees correction parameter), and ξ. Details of these calculations are described elsewhere.[4] The dimensions of the matrices are the following: Γ_6, 20×20; Γ_7, 22×22; and Γ_8, 42×42.[5] Values of B, C, Dq, and α used in these calculations were obtained by fitting to the observed band energies in the spectrum taken at 77°K, and the values are 840, 3080, 780, and 76 cm^{-1},