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Excited State Wave Functions

I. Comparison of the Messmer and Rayleigh-Ritz Variational Methods in the Case of Hydrogen

A. C. BRETT and T. W. DINGLE

Department of Chemistry, University of Victoria, Victoria, B. C., Canada

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Wave functions and energies were calculated for the $2s$, $3p_0$, and $4d_0$ states of the hydrogen atom using the Messmer and Rayleigh-Ritz variational methods with minimization of the second eigenvalue. The wave functions were linear expansions of Gaussian functions and both linear and exponential parameters were varied. Except for the two term expansions, calculated values of the energies and expectation values, $\langle r^{-1}\rangle$, $\langle r\rangle$ and $\langle r^2\rangle$ were within two percent of the true values for both methods.

1. Introduction

A variational method for obtaining the wave functions of excited states has been proposed recently by Messmer [1, 2]. He has stated that this method is free from the restriction that the excited state wave function must be orthogonal to all the true wave functions of states of the same symmetry and of lower energy. The basis of the method is a minimization of the quantity ε^2/Δ where $\varepsilon = E - W$ and $\Delta = \langle\Phi|(\boldsymbol{H}-E)^2|\Phi\rangle$. $E = \langle\Phi|\boldsymbol{H}|\Phi\rangle$ where $\boldsymbol{H}$ denotes the true Hamiltonian, W the true energy, and Φ an approximate wave function for the excited state.

Messmer has argued that minimization of ε^2/Δ produces a wave function which is the best approximation to the true wave function for the system over the whole of configuration space, i. e., that the overlap between the true and approximate wave function is maximized. He has also suggested that a possible criterion for testing the validity of this contention is comparison of the values of the quantities $\langle \boldsymbol{r}^{-1}\rangle$, $\langle \boldsymbol{r}\rangle$ and $\langle \boldsymbol{r}^2\rangle$, computed from the approximate wave function, with known values for these quantities.

The purpose of the work described here was to investigate the Messmer method as applied to a simple system. We chose to work with the hydrogen atom, using Gaussian-type functions of the form:

$$\Phi_{l,m} = \sum_i c_i r^l \exp(-\eta_i r^2)\, Y_{l,m}(\theta, \phi) \tag{1}$$

to approximate the $2s$, $3p_0$ and $4d_0$ states. The hydrogen atom seemed to be a reasonable system to study since it is simple and exact values for W, $\langle \boldsymbol{r}^{-1}\rangle$, $\langle \boldsymbol{r}\rangle$ and $\langle \boldsymbol{r}^2\rangle$ are known. Moreover, there is at present, considerable interest in the use of Gaussian-type functions to approximate molecular wave functions.

2. Application of the Messmer Method

Since the approximate wave functions (1) are not normalized, E and Δ must be defined so as to include the overlap integral. Therefore,

$$E = \langle \boldsymbol{H} \rangle / \langle \boldsymbol{S} \rangle$$

and

$$\Delta = \langle \boldsymbol{H}^2 \rangle / \langle \boldsymbol{S} \rangle - E^2 , \tag{2}$$

where $\langle \boldsymbol{H} \rangle = \langle \Phi_{l,m} | \boldsymbol{H} | \Phi_{l,m} \rangle$, $\langle \boldsymbol{H}^2 \rangle = \langle \Phi_{l,m} | \boldsymbol{H}^2 | \Phi_{l,m} \rangle$ and $\langle \boldsymbol{S} \rangle = \langle \Phi_{l,m} | \Phi_{l,m} \rangle$. The condition that ε^2/Δ be minimal, *viz.*, $\delta(\varepsilon^2/\Delta) = 0$, gives

$$2\delta\varepsilon - (\varepsilon/\Delta)\,\delta\Delta = 0 . \tag{3}$$

Now

$$\varepsilon = \langle \boldsymbol{H} \rangle / \langle \boldsymbol{S} \rangle - W$$

and

$$\Delta = \langle \boldsymbol{H}^2 \rangle / \langle \boldsymbol{S} \rangle - (\langle \boldsymbol{H} \rangle / \langle \boldsymbol{S} \rangle)^2 ,$$

therefore, for a given W we have

$$\delta\varepsilon = \delta \langle \boldsymbol{H} \rangle / \langle \boldsymbol{S} \rangle - (\langle \boldsymbol{H} \rangle / \langle \boldsymbol{S} \rangle^2)\, \delta \langle \boldsymbol{S} \rangle \tag{4}$$

and

$$\begin{aligned} \delta\Delta = {} & \delta \langle \boldsymbol{H}^2 \rangle / \langle \boldsymbol{S} \rangle - (\langle \boldsymbol{H}^2 \rangle / \langle \boldsymbol{S} \rangle^2)\, \delta \langle \boldsymbol{S} \rangle - 2(\langle \boldsymbol{H} \rangle / \langle \boldsymbol{S} \rangle^2)\, \delta \langle \boldsymbol{H} \rangle \\ & + 2(\langle \boldsymbol{H} \rangle^2 / \langle \boldsymbol{S} \rangle^3)\, \delta \langle \boldsymbol{S} \rangle . \end{aligned} \tag{5}$$

Substitution of (4) and (5) into (3) gives

$$2\delta \langle \boldsymbol{H} \rangle - (E + W)\, \delta \langle \boldsymbol{S} \rangle - (\varepsilon/\Delta)\, (\delta \langle \boldsymbol{H}^2 \rangle - 2E\delta \langle \boldsymbol{H} \rangle + E^2 \delta \langle \boldsymbol{S} \rangle) = 0 \tag{6}$$

after rearrangement.

To find the trial function which satisfies Eq. (6), the exponential parameters, η_i, and the linear coefficients, c_i, are varied in a nested fashion. The exponential parameters are varied by a direct (pattern) search technique [3]. For each set of values given for the η_i by the search routine, ε^2/Δ is minimized with respect to the c_i. This latter process yields in each case, a set of linear equations of which the following is the i^{th} member:

$$\begin{aligned} \sum_j c_j \{ & 2H_{ij} + 2H_{ji} - (E + W)\,(S_{ij} + S_{ji}) \\ & - (\varepsilon/\Delta)\, [H_{ij}^2 + H_{ji}^2 - 2E(H_{ij} + H_{ji}) + E^2(S_{ij} + S_{ji})] \} = 0 , \end{aligned} \tag{7}$$

where

$$H_{ij} = \langle \phi_{l,m}^i | \boldsymbol{H} | \phi_{l,m}^j \rangle , \quad H_{ij}^2 = \langle \phi_{l,m}^i | \boldsymbol{H}^2 | \phi_{l,m}^j \rangle ,$$

$S_{ij} = \langle \phi_{l,m}^i | \phi_{l,m}^j \rangle$ and $\phi_{l,m}^i$ denotes the i^{th} term in (1). If E were known, then the equations represented by (7) could be solved immediately as an eigenvalue problem of the form $(\boldsymbol{A} - (\varepsilon/\Delta)\, \boldsymbol{B})\, \boldsymbol{C} = 0$, or

$$(\boldsymbol{B}^{-1} \boldsymbol{A} - (\varepsilon/\Delta)\, \boldsymbol{I})\, \boldsymbol{C} = 0 , \tag{8}$$

where the elements of the arrays $\boldsymbol{A}$ and $\boldsymbol{B}$ have the form

$$A_{ij} = 2H_{ij} + 2H_{ji} - (E + W)\,(S_{ij} + S_{ji}) ,$$

$$B_{ij} = H_{ij}^2 + H_{ji}^2 - 2E(H_{ij} + H_{ji}) + E^2(S_{ij} + S_{ji})$$

and where $\boldsymbol{C}$ denotes the array of linear coefficients.

Since E is not known *a priori*, an iterative calculating procedure must be employed. For an initial trial E, (8) is solved for (ε/Δ) and the array of coefficients $\boldsymbol{C}$. The vector of coefficients corresponding to the *second* lowest eigenvalue (ε/Δ) is selected from $\boldsymbol{C}$. These coefficients are used to compute another value for E according to Eq. (2). This new E is then used to solve (8) again. The procedure just described is repeated until the trial E and the next calculated value of E are consistent. ε^2/Δ is then calculated. The exponential parameters are changed by the search routine and the iterative procedure is repeated. This nested variation of the linear and non-linear parameters is continued until ε^2/Δ attains a stationary value.

Table 1. Results obtained with the Messmer method

	E	$\langle r^{-1}\rangle$	$\langle r\rangle$	$\langle r^2\rangle$
$2s$ orbital				
2 terms	-0.1164	0.2451	6.141	44.68
3 terms	-0.1236	0.2493	5.993	41.73
4 terms	-0.1246	0.2502	5.966	41.19
true	-0.1250	0.2500	6.000	42.00
$3p_0$ orbital				
2 terms	-0.05367	0.1094	12.59	183.9
3 terms	-0.05533	0.1108	12.46	177.9
4 terms	-0.05546	0.1111	12.43	176.6
true	-0.05556	0.1111	12.50	180.0
$4d_0$ orbital				
2 terms	-0.03058	0.06162	21.09	510.3
3 terms	-0.03118	0.06240	20.92	497.5
4 terms	-0.03121	0.06244	20.90	496.3
true	-0.03125	0.06250	21.00	504.0

The proceeding procedure was carried out using 2, 3 and 4 term expansions of the type given by Eq. (1) to describe each of the $2s$, $3p_0$ and $4d_0$ states of the hydrogen atom. The appropriate known true value for W was used in each case. The functions thus determined were used to calculate values for $\langle r^{-1}\rangle$, $\langle r\rangle$ and $\langle r^2\rangle$. The results are given in Table 1.

The reason for choosing the second eigenvalue was to ensure that the approximate wave function approached the true wave function for the excited state under consideration as ε^2/Δ approached zero. Messmer points out that both ε^2 and Δ must approach zero as ε^2/Δ approaches zero if the approximate wave function is to be reasonably close to the true wave function. Some calculations were done using the vector of coefficients associated with the lowest eigenvalue and these gave very poor wave functions. In this case ε^2 can be made equal to zero, but Δ is not approaching zero in any reasonable manner; hence, the above criteria are not satisfied. These results emphasize the need for choosing the appropriate eigenvalue.

3. Application of the Rayleigh-Ritz Method

The results obtained with the Messmer method as outlined above, were compared with wave functions of the form (1), calculated from a modification of the Rayleigh-Ritz variational method. Variation of the linear and non-linear (exponential) parameters was again carried out in a nested fashion. For each set of the exponential parameters given by the direct search routine, secular equations of the form

$$(\boldsymbol{S}^{-1}\boldsymbol{H}-E\boldsymbol{I})\boldsymbol{C}=0 \tag{9}$$

were solved for the eigenvalues, E, and the eigenvectors, $\boldsymbol{C}$ ($\boldsymbol{H}$, $\boldsymbol{S}$ and $\boldsymbol{I}$ denote the Hamiltonian, Gram and identity matrices respectively). The exponential parameters were varied and Eq. (9) was solved for each variation until a minimal second lowest eigenvalue was achieved. The vector of coefficients corresponding to the second eigenvalue was selected from $\boldsymbol{C}$. The wave function thus determined was used to compute values for $\langle r^{-1}\rangle$, $\langle r\rangle$ and $\langle r^2\rangle$ which are reported in Table 2. The energy values obtained for the 2*s* state are identical to those reported by Reeves [4] using a similar method and very similar expansions.

Table 2. Results obtained with the Rayleigh-Ritz method

	E	$\langle r^{-1}\rangle$	$\langle r\rangle$	$\langle r^2\rangle$
2*s* orbital				
2 terms	−0.1168	0.2340	6.355	47.68
3 terms	−0.1237	0.2479	6.016	42.04
4 terms	−0.1246	0.2491	5.982	41.41
true	−0.1250	0.2500	6.000	42.00
$3p_0$ orbital				
2 terms	−0.05369	0.1074	12.82	190.8
3 terms	−0.05533	0.1104	12.49	178.6
4 terms	−0.05547	0.1108	12.45	177.1
true	−0.05556	0.1111	12.50	180.0
$4d_0$ orbital				
2 terms	−0.03059	0.06116	21.29	520.4
3 terms	−0.03118	0.06236	20.94	498.6
4 terms	−0.03121	0.06242	20.92	496.9
true	−0.03125	0.06250	21.00	504.0

4. Discussion and Conclusions

The percentage deviation of the calculated value from the true value was determined in each case for $\langle r^{-1}\rangle$, $\langle r\rangle$ and $\langle r^2\rangle$. These values are recorded in Table 3. Examination of this table shows that the Messmer method, as described in Section 2, gives better results for the calculated quantities with the two term expansions than does the Rayleigh-Ritz method. Moreover, it yields better results for $\langle r^{-1}\rangle$ with the three and four term expansions. However, on the whole the Rayleigh-Ritz method gives better results for $\langle r\rangle$ and $\langle r^2\rangle$. Thus it would seem that the Messmer method yields wave functions which are better in the vicinity of the nucleus. This conclusion was confirmed by calculating the root mean square

Table 3. Percentage deviation of calculated values of $\langle r^{-1}\rangle$, $\langle r\rangle$ and $\langle r^2\rangle$ from the true values using the Messmer and Rayleigh-Ritz wave functions

	$\langle r^{-1}\rangle$		$\langle r\rangle$		$\langle r^2\rangle$	
	Messmer	Rayleigh-Ritz	Messmer	Rayleigh-Ritz	Messmer	Rayleigh-Ritz
2*s* orbital						
2 terms	−1.96	−6.40	2.35	5.92	6.38	13.5
3 terms	−0.28	−0.84	−0.12	0.27	−0.64	0.10
4 terms	0.08	−0.36	−0.57	−0.30	−1.93	−1.40
$3p_0$ orbital						
2 terms	−1.53	−3.33	0.72	2.56	2.17	6.00
3 terms	−0.27	−0.63	−0.32	−0.08	−1.17	−0.78
4 terms	0.00	−0.27	−0.56	−0.40	−1.89	−1.61
$4d_0$ orbital						
2 terms	−1.41	−2.14	0.43	1.38	1.25	3.25
3 terms	−0.16	−0.22	−0.38	−0.28	−1.29	−1.07
4 terms	−0.10	−0.13	−0.48	−0.38	−1.53	−1.41

Table 4. Overlap of approximate with true wave function

	Rayleigh-Ritz Method	Messmer Method
2*s* orbital		
2 terms	0.992152	0.994997
3 terms	0.999287	0.999324
4 terms	0.999339	0.999322
$3p_0$ orbital		
2 terms	0.994861	0.996927
3 terms	0.999256	0.999255
4 terms	0.999174	0.999159
$4d_0$ orbital		
2 terms	0.995887	0.997130
3 terms	0.999196	0.999180
4 terms	0.999117	0.999105

deviation of the wave function from the true wave function in the vicinity of the nucleus. Again the Messmer method yielded a better wave function, indicating that the Messmer functions fit the true wave function better in the least squares sense in this region.

Another criterion for assessing the goodness of the approximate wave functions is to calculate the overlap between the approximate and the true wave function. The results of such calculations are shown in Table 4. They show that the Messmer method gives significantly better wave functions only for the two term expansion.

Except for the results obtained with the two term expansion, the Messmer method as we have applied it, does not seem to give significantly better wave functions compared to those obtained with the Rayleigh-Ritz method. In view of the much greater amount of effort required in using the Messmer method, as measured in terms of computer time and preliminary mathematical manipulation, there is some question in our minds as to its superiority over some modification of the established variational method.

One possible approach is suggested by the method we used to obtain the excited states within the context of the Rayleigh-Ritz method. If a wave function is approximated by a linear combination of functions, then substitution of this approximation into the expression for the energy, followed by minimization of the energy with respect to the linear parameters, leads to the familiar secular equation. If there are N linear terms, then there will be N solutions to the secular equation. It can be shown [5] that the k^{th} lowest eigenvalue is an upper bound to the k^{th} lowest state of the symmetry under consideration. Usually, the non-linear (exponential) parameters are varied so as to give the lowest possible value for the lowest eigenvalue. This leads to the best possible basis set of the given mathematical form for the lowest state. However, it is unlikely that this will be a good basis set to represent the excited states. If the appropriate eigenvalue is minimized with respect to the non-linear parameters, then it should produce the best basis set to represent the excited state.

Our calculations show that this is true for the hydrogen atom. Hylleraas [6] has carried out variational calculations of this type on the helium atom and obtained reasonable energies for the excited state. Recently, Bishop *et al.* [7, 8] have done calculations on some excited states of H_2O and NH_3 using one-center multiconfigurational wave functions containing orthogonalized Slater type functions. They have minimized the appropriate eigenvalue with respect to the exponential parameters for each state. They obtained the correct order for the states and the energy differences between the states were quite reasonable. Moreover, the predicted nuclear geometries were consistent with the known experimental data. Some unpublished data of ours on the He atom indicate that the energies for the excited states are better than for the ground state to the same level of approximation. We are continuing to explore this method of obtaining excited states.

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Prof. Thomas Dingle
University of Victoria
Department of Chemistry
Victoria, British Columbia, Canada