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ON THE TRUNCATION SCHEME FOR THE HYPERSPHERICAL HARMONICS EXPANSION BASIS FOR TWO–ELECTRON ATOMS

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In spite of the fact that the usual hyperspherical harmonics expansion method has a number of advantages, the rate of convergence is quite slow for diffused atomic systems interacting through long–range Coulomb forces. An efficient truncation scheme of the basis, in which only $l_1 = 0$ partial waves for $K > K_{M_1}$, are retained is proposed. This results in a marginal increase in computation beyond that for K_{M_1}. Calculation of various quantities indicate that the truncation scheme is particularly useful for diffused atomic systems.

1. *Introduction*

Available experimental results as well as multiparameter variational calculations [1,2] for atomic bound systems are extremely precise. There are several other theoretical approaches for studying the bound states of few–electron atoms. Among these, the hyperspherical harmonic expansion (HHE) method has certain advantages. Based on first principles, it provides a solution of the nonrelativistic Schrödinger equation which is essentially exact, in the sence that there are no approximations other than an inevitable truncation of the expansion basis. Provided computation facilities are adequate and adopted numerical codes are efficient, one can, in principle, demand any preset precision, by appropriately truncating the basis. Furthermore, a clear physical picture of the system in terms of the configuration space wave function is possible. On the other hand, the convergence of the

binding energy (BE) with respect to addition of higher partial waves is slow for the long–range Coulomb potential. This demands solving a large number of coupled differential equations (CDE) for a specified precision. The number of CDE increases rapidly with the inclusion of higher partial waves. Thus inclusion of additional partial waves requires extremely time consuming and tricky numerical algorithms. Limitations of computer facility and numerical algorithms set a rather severe limitation on the precision attainable by the HHE method. It is our endeavour in this communication to show that truncation in appropriate physical quantities (not in hyperangular momentum but in relative orbital angular momenta), coupled with the use of convergence theorems on HHE, can lead to sufficiently high precision, even with a fairly small–sized computer.

In an earlier calculation [3], we applied the hyperspherical harmonic expansion method (HHEM) to various two–electron atoms achieving a good degree of success. In that calculation, no truncation in the expansion basis was made for all partial waves upto and including a limiting grand orbital quantum number K_M; then theorems [4] on convergence of hyperspherical harmonics (HH) basis were utilized to extrapolate the calculated BE for various K_M values to obtain a converged BE. The accuracy of this procedure depends on (1) the accuracy of the calculated BE for a given K_M, and (2) whether such K_M values are large enough to be already in the asymptotic K region satysfying the convergence theorems. Sufficient attention was paid to the first criterion in the earlier calculation [3], but limitations of computer facility restricted us to $K_M \leq 20$, with little possibility of a precise verification whether the asymptotic K region was attained for these values of K_M. In the present work we investigate this point more carefully.

2. HHE method

The nonrelativistic Hamiltonian of a two–electron atom (disregarding the motion of the nucleus), is

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \tag{1}$$

where $\vec{r}_i$ is the position of the i-th electron ($i = 1, 2$), r_{12} is the relative separation between the electrons, Z the charge of the nucleus, and atomic units are chosen such that $m = e = \hbar = 1$. The wave function for the ground state of the system is expanded in HH basis $\{\mathcal{Y}_{K,l_1}(\Omega)\}$;

$$\Psi(\vec{r}_1, \vec{r}_2) = \sum_{Kl_1} \rho^{-5/2} \mathcal{U}_{Kl_1}(\rho) \mathcal{Y}_{K,l_1}(\Omega), \tag{2}$$

where $\rho = \sqrt{r_1^2 + r_2^2}$ is the hyperradius and $\Omega = \{\hat{r_1}, \hat{r_2}, \phi\}$, $\phi = \tan^{-1}(r_1/r_2)$ represent the hyperangles. The quantity K is the grand orbital quantum number and l_i the orbital angular momentum of the i-th electron. For the ground state of

this system, the spin wave function of the two electrons is singlet, and consequently Ψ should be symmetric under the exchange of the positions of the two electrons. From the properties [5] of the HH ($\mathcal{Y}_{K,l_1,l_2,L,M}(\Omega)$), this requirement is satisfied if $n = (K - l_1 - l_2)/2$ is an even integer ≥ 0. For the ground state, the total orbital angular momentum $L = 0$ ($\vec{L} = \vec{l_1} + \vec{l_2}$). Thus $l_1 = l_2$, and each takes nonnegative even or odd integral values $\leq K/2$, when $K/2$ is even or odd, respectively. Quantum numbers $l_2 (= l_1)$ and $L = M = 0$ have been suppressed in Eq. (2). An expression for $\mathcal{Y}_{K,l_1}(\Omega)$ can be found in Ref. 3. Substitution of Eq. (2) in the Schrödinger equation, and projection onto a particular HH leads to a set of CDE for the hyperradial partial waves $\mathcal{U}_{Kl_1}(\rho)$

$$\left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + \frac{\mathcal{L}(\mathcal{L}+1)}{\rho^2} - E\right]\mathcal{U}_{Kl_1}(\rho)$$

$$+\sum_{K'l_1'}\left\langle \mathcal{Y}_{Kl_1}(\Omega)\left|-\frac{1}{\rho}\left(\frac{1}{\cos\phi}+\frac{1}{\sin\phi}\right)\right|\mathcal{Y}_{K'l_1'}(\Omega)\right\rangle \mathcal{U}_{K'l_1'}(\rho)+$$

$$\sum_{K'l_1'}\left\langle \mathcal{Y}_{Kl_1}(\Omega)\left|\frac{1}{\rho}\frac{1}{\sqrt{\sin^2\phi+\cos^2\phi-2\sin\phi\cos\phi\cos\beta}}\right|\mathcal{Y}_{K'l_1'}(\Omega)\right\rangle \mathcal{U}_{K'l_1'}(\rho) = 0, \tag{3}$$

where $\mathcal{L} = K + 3/2$ and β is the angle between $\vec{r}_1$ and $\vec{r}_2$.

3. Numerical procedure

The matrix elements are reduced analytically to a single integral over ϕ and are calculated for $\rho = 1$ by 32–point Gaussian quadrature for each subinterval, there being sufficient number of subintervals to ensure a precision of 1 in 10^{10} in a double precision calculation. These matrices are stored and used to calculate the matrix elements for a given ρ value. The system of CDE is then solved by renormalized Numerov (RN) method [6,7] to obtain the binding energy, $-E$, and partial waves, $\mathcal{U}_{Kl_1}(\rho)$. In the earlier calculation [3], all allowed l_1 values for a given K were included in the basis expansion and K was restricted to $K \leq K_M$. However, in the course of the present investigation, we find, as one expects intuitively, that for a given K, the contribution for $l = 0$ partial wave is the largest (provided $K/2$ is even) and that for higher l_1 values decreases rapidly as l_1 increases. The absolute probability of a given (Kl_1) partial wave become $< 10^{-6}$ for $l_1 > 0$ and $K > K_{M_1}$ ($K_{M_1} = 12$ for He and 16 for H^-). The total number of (Kl_1) partial waves for a given K_M is

$$N = \left\{ \begin{array}{cc} (K_M/4+1)^2 & \text{if } K_M/2 \text{ is even} \\ (K_M/2+1)(K_M/2+3)/4 & \text{if } K_M/2 \text{ is odd} \end{array} \right\}. \tag{4}$$

Hence the number (N) of CDE for a given K_M, increases rapidly with K_M. Since the computation time increases as the cube of the number of CDE, one sees that

for sufficiently large K_M, CPU time increases as the sixth power of K_M. However, contributions of $l_1 \neq 0$ for $K > K_{M_1}$ being sufficiently small, we now follow a truncation scheme in which all allowed l_1 values for $K \leq K_{M_1}$ and only $l_1 = 0$ for $K_{M_1} < K \leq K_{M_2}$ are included. This procedure increases the number of CDE only marginally beyond that for K_{M_1} (only one additional partial wave for only those K values ($> K_{M_1}$) which are multiples of 4). This results in a manageable increase in memory, CPU time and complexity of numerical algorithm. On the other hand, with this minimal increase in computation, almost all the effects of higher K values ($> K_{M_1}$) are taken care of and so one can reach the asymptotic K region, making the extrapolation formula more reliable.

In the present work, we have also paid careful attention to the correct behaviour of the partial waves as ρ tends to zero, as also the precise choice of an upper cut–off ρ value (ρ_∞). The former is necessary since the numerical calculation must exclude the point $\rho = 0$ (which is a singularity for the Coulomb potential) and it is replaced by a lower cut–off value ρ_0. At ρ_0, the partial waves do not vanish exactly. They have been replaced by an approximate analytic expression obtained from Eq. (3), and the initial $[R_0^{-1}]$ matrix necessary in the RN method [6,7] has been modified accordingly. This, however, makes an insignificant change in BE (ρ_0 has been chosen to be 0.001 au).

TABLE 1.
Effect of increasing ρ_∞ (all l_1 values for a given K included).

K_M	ρ_∞ (atomic units)	BE (atomic units)	
		H^- ion	He atom
12	12	0.5125769932	2.8760085122
	17	0.5125598539	2.8760085122
	27	0.5125598242	2.8760085122
	77	0.5125598242	2.8760085122
16	12	0.5177256545	2.8875442205
	17	0.5177059826	2.8875442205
	27	0.5177059247	2.8875442205
	77	0.5177059247	2.8875442205
20	12	0.5207346671	2.8935847030
	17	0.5207196822	2.8935847030
	27	0.5207196150	2.8935847030
	77	0.5207196150	2.8935847030

For the choice of ρ_∞, especially for a loosely bound system like H^- ion, we compare the BE calculated for various ρ_∞ values. The computation time increases proportionately as ρ_∞ is increased, if ρ–mesh size (h) is kept the same. On the other hand, for sufficiently large ρ, a given partial wave varies slowly with ρ and hence h can be increased. We have divided the ρ space in several blocks, each block having uniform mesh size. The blocks are chosen to be 0–12, 12–17, 17–27, 27–77, with mesh sizes 0.02, 0.05, 0.1 and 0.5, respectively (in atomic units). Calculations performed for a loosely bound system (H^- ion), as also a fairly strongly bound

system (He–atom), are presented in Table 1. From this, one can conclude that sufficiently accurate BE is obtained with the choice $\rho_\infty = 27$ au for H^- ion and $\rho_\infty = 12$ au for He atom for a reliability upto the ninth significant digit in the BE. Furthermore, a cut–off of $\rho_\infty = 12$ au for H^- ion will introduce an error in the fifth significant digit.

4. *Truncation scheme*

With the values of ρ_0 and ρ_∞ fixed, we direct our attention to contribution of partial waves with $l_1 \neq 0$. Table 2 presents the probabilities of various partial waves for $K_M = 20$ for the two chosen systems. One notices that $l_1 = 0$ or $l_1 = 1$ partial waves contribute the most, if $K/2$ is even or odd, respectively, the contribution decreasing steadily with increase of K. Other small l_1 values also contribute significantly for $K < K_{M_1}$ ($K_{M_1} = 12$ for He and 16 for H^-), however for $K > K_{M_1}$ only $l_1 = 0$ terms have any appreciable contribution ($> 10^{-6}$).

TABLE 2.
Probabilities of various partial waves for $K_M = 20$.

K	l_1	Probability		K	l_1	Probability	
		H^- ion	He atom			H^- ion	He atom
0	0	0.63455685	0.92021381	14	5	0.00000003	0.00000008
2	1	0.00888331	0.00417341		7	0.00000013	0.00000025
4	0	0.27030521	0.06555545	16	0	0.00460655	0.00038362
	2	0.00019659	0.00018739		2	0.00000003	0.00000001
6	1	0.00038605	0.00001118		4	0.00000002	0.00000002
	3	0.00001966	0.00002523		6	0.00000003	0.00000004
8	0	0.06361362	0.00780588		8	0.00000008	0.00000012
	2	0.00000217	0.00000051	18	1	0.00000060	0.00000003
	4	0.00000365	0.00000558		3	0.00000002	0.00000000
10	1	0.00003467	0.00000203		5	0.00000003	0.00000001
	3	0.00000003	0.00000036		7	0.00000005	0.00000002
	5	0.00000096	0.00000166		9	0.00000012	0.00000006
12	0	0.01596311	0.00151243	20	0	0.00142017	0.00011969
	2	0.00000029	0.00000012		2	0.00000010	0.00000000
	4	0.00000003	0.00000018		4	0.00000015	0.00000000
	6	0.00000032	0.00000060		6	0.00000026	0.00000001
14	1	0.00000396	0.00000006		8	0.00000034	0.00000001
	3	0.00000003	0.00000005		10	0.00000079	0.00000003

Next, we investigate the effect on the BE of truncating all l_1 values to a maximum of l_M for each $K \leq K_M$. The results are presented in Table 3. The last entry for a given K_M, represents the BE obtained with the full expansion basis for that K_M. The table vividly depicts how the contribution of larger l_1 values to the BE for a given K_M decreases rapidly with l_1. But the increment in BE due to the increase

of l_M from one value to the next is nearly independent of K_M (especially for larger l_M). This shows that the contributions of small l_1 partial waves come mostly from smaller K_M values.

TABLE 3.
Calculated BE (au) for various K_M including all $l_1 \leq l_M$.

System	l_M	BE			
		$K_M = 8$	$K_M = 12$	$K_M = 16$	$K_M = 20$
H^-	0	0.48427753	0.49553911	0.50144488	0.50502527
	1	0.50113333	0.51117763	0.51635119	0.51940270
	2	0.50225380	0.51221600	0.51735371	0.52037352
	3	0.50249379	0.51244131	0.51757366	0.52058606
	4	0.50257359	0.51251658	0.51764793	0.52065764
	5		0.51254577	0.51767902	0.52068797
	6		0.51255982	0.51769434	0.52070295
	7			0.51770590	0.52071089
	8			0.51772600	0.52071556
	9				0.52071802
	10				0.52073626
He	0	2.8243475	2.8506398	2.8623890	2.8685927
	1	2.8470786	2.8728177	2.8843216	2.8903669
	2	2.8494575	2.8751293	2.8866163	2.8926444
	3	2.8500205	2.8756923	2.8871806	2.8932046
	4	2.8502159	2.8758909	2.8873813	2.8934039
	5		2.8759698	2.8874677	2.8934910
	6		2.8760085	2.8875111	2.8935345
	8			2.8875320	2.8935725
	10				2.8935787

Observations of Tables 2 and 3 suggest that our proposed truncation scheme, viz, retaining all allowed partial waves for $K \leq K_{M_1}$, and only $l_1 = 0$ partial waves for $K_{M_1} < K < K_{M_2}$, would be quite beneficial. As mentioned earlier, this scheme increases the number of CDE and hence the memory and CPU requirements only marginally, while allowing fairly large K_{M_2} values, which will be in asymptotic K region. Calculated BE following this truncation scheme with $K_{M_1} = 20$ and various values of K_{M_2} are presented in Table 4. We next use these calculated BE to extrapolate the converged BE. According to the theorems on convergence of hyperspherical harmonics expansion [4], one expects the following relation to hold [3]

$$(K_M + x)^4 \Delta B_{K_M} = C, \tag{5}$$

where

$$\Delta B_{K_M} = B_{K_M+4} - B_{K_M}, \tag{6}$$

B_{K_M} being the BE calculated with a particular K_M value; C and x are two constants determined by fitting two successive ΔB_{K_M} values. Once these two constants are known, Eq. (5) can be used to calculate extrapolated B_{K_M} for $K_M > K_{M_2}$ for any K_{M_2}. Thus, one can obtain extrapolated BE for a fairly large $K_M (= K_{M_3})$ and the final missing BE from $K_M = K_{M_3}$ to $K = \infty$ can be estimated as

$$\Delta = \sum_{K=K_{M_3}}^{\infty} \Delta B_K = \sum_{n=0}^{\infty} \frac{C}{(K_{M_3} + 4n + x)^4} \approx \frac{C}{12(K_{M_3} + x)^3}. \tag{7}$$

TABLE 4.
Calculated BE (au) *including all allowed* l_1 *for* $K \leq K_{M_2}$ *and only* $l_1 = 0$ *for* $K_{M_1} < K \leq K_{M_2}$.

System	K_{M_1}	K_{M_2}	BE
H^-	20	24	0.5225750089
		28	0.5237949184
		32	0.5246226565
		36	0.5252072535
He	20	24	2.896944959
		28	2.898992302
		32	2.900287562
		36	2.901155281

Equation (5), together with Eq. (7) have been used to extrapolate the fully converged $K \to \infty$ BE for both the systems for each triad of three successive K_M values (each a multiple of 4) and are presented in Table 5. One observes that the converged BE for each triad of K_M–values oscillates and approaches a converged value as K_M increases. In the present truncation scheme, as K_M increases beyond 20, two effects become important: on the one hand, asymptotic K region is gradually reached; on the other hand, the small but finite missing BE due to $K > 20$, $l_1 \neq 0$ partial waves accumulate. While the nonattainment of asymptotic K region will have a tendency to produce large extrapolated BE, the missing $l_1 \neq 0$ partial waves will produce a smaller BE. Due to the former reason, an extrapolation to $K_M \to \infty$ using calcualted BE with all l_1–partial wave for $K_M \leq 20$, would produce the BE to be too large. For this reason, in our earlier work [3] we had to stop the extrapolation to such a K_M, that corresponding ΔB_{K_M} was of the order of the estimated error in the extrapolation formula (0.00005 au). A close scrutiny of Table 5 reveals that the $K_M \to \infty$ extrapolated BE attains a convergence as K_M of the triad increases. This is due to a gradual attainment of the asymptotic K region. The cummulative loss of $l_1 \neq 0$ contributions for $K_M > 20$ will be the eventual error in the converged BE according to the present scheme. The extrapolated BE for the last entry of each system in Table 5 differs by 0.087% and 0.002%, respectively, from the accurate multiparameter variational calculation of Pekeris [8–11]. While the latter is of the same order as that obtained in our previous calculation [3], the error for H^- is significantly less (0.087% as compared with 0.2% in the earlier

calculation). Since the H^- is a diffused system, larger K values contribute to the ground state and the present truncation scheme is especially beneficial. The largest value of K_{M_2}, used in the present work is 36, for which the number of CDE is 40 and 100, respectively, for the present truncation scheme and no truncation at all. Thus, the CPU time has been reduced by a factor of 16, with minimal loss of precision. Memory requirement is also reduced by a factor of 6.25.

TABLE 5.
Extrapolated BE using the data of Tables 3 and 4.

System	Extrapolation based on K_M values	Extrapolated BE
H_	8,12,16	0.526731
	12,16,20	0.527300
	16,20,24	0.526999
	20,24,28	0.527395
	24,28,32	0.527206
	28,32,36	0.527278
He	8,12,16	2.903507
	12,16,20	2.904381
	16,20,24	2.903645
	20,24,28	2.903881
	24,28,32	2.903674
	28,32,36	2.903779

5. *Conclusion*

We have proposed here a truncation scheme for the HH expansion, where all l_1 partial waves for $K \leq K_{M_1}$ and only $l_1 = 0$ partial waves for $K_{M_1} < K \leq K_{M_2}$, are retained. Since the number of l_1 partial waves for a given K value increases very rapidly, this truncation scheme reduces the number of CDE drastically. Table 6 shows the reduction factors of memory and CPU time requirements for various representative values of K_{M_2}. Large K_M values are essential for diffused and extended systems like H^-, Ps^- etc. We conclude that the proposed truncation scheme is very beneficial for such diffused systems.

TABLE 6.
Benefits of the proposed truncation scheme for representative values of K_{M_2} ($K_{M_1} = 20$).

K_{M_2}	Number of CDE		Reduction factor in	
	No truncation	Truncated space	Memory	CPU time
36	100	40	6.25	15.625
40	121	41	8.71	25.704
48	169	43	15.45	60.709
60	256	46	30.97	172.364
100	676	56	145.72	1759.041

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OGRANIČENA BAZA RAZVOJA HIPERSFERIČNIH HARMONIKA ZA DVOELEKTRONSKE ATOME

Uobičajena metoda razvoja po hipersferičnim harmonicima ima mnoge prednosti, međutim, konvergencija je vrlo spora za proširene atomske sustave koji međudjeluju dugodosežnim Coulombovim silama. Predlaže se učinkovito ograničenje razvoja u kojem se zadržavaju samo parcijalni valovi $l_1 = 0$ za $K > K_{M_1}$.