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Systematic Sequences of Even-tempered Gaussian Primitives in Electron Correlation Studies Using Many-Body Perturbation Theory

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The use of systematic sequences of even-tempered Gaussian primitive functions in electron correlation studies using diagrammatic many-body perturbation theory is examined. The "*s* limit" electronic energy of the Be atom and the '*sp* limit" energy of the Ne atom have been computed as examples. The use of the Hartree extrapolation procedure to obtain empirical upper bounds for the basis set limit is investigated. The empirical lower bound for the basis set limit suggested by Schmidt and Ruedenberg is examined for calculations which include electron correlation.

Key words: Basis set – Even-tempered basis set – Universal basis set – Correlation energy – Many-body perturbation theory.

1. Introduction

The choice of basis set in studies of atomic and molecular systems ultimately determines the accuracy of the calculations. Within the Hartree–Fock molecular orbital model, empirical recipes for choosing basis sets are well established for both Slater exponential functions [1] and Gaussian functions [2]. The best choice of basis sets for calculations which take account of electron correlation effects is not so well documented.

The concept of an even-tempered basis set has been shown to be of great value in atomic and molecular studies [3–15]. Even-tempered basis functions span the one-electron space in a fairly uniform fashion. They allow fairly large basis sets to be generated while avoiding linear dependence. Raffenetti [8] was, for example,

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able to devise Slater basis sets for heavy atoms using the even-tempered concept with relatively modest computing effort.

Feller and Ruedenberg [9] and Schmidt and Ruedenberg [10] have recently devised schemes for systematically extending basis sets of the even-tempered type. They have applied the scheme to a number of atomic systems using sets of Gaussian primitive functions with the Hartree–Fock molecular orbital model. This systematic approach enables the convergence of the calculations with respect to basis set to be examined and the basis set limit estimated. It appears that it is possible to derive empirical lower bounds and empirical upper bounds to the basis set limit by making assumptions about the convergence properties with respect to basis set size.

In this paper we examine the application of the systematic scheme for extending basis sets devised by Ruedenberg and his collaborators to calculations which include electron correlation effects. The diagrammatic many-body perturbation theory [16] is used to account for electron correlation. This approach currently forms the basis of one of the most accurate treatments of electron correlation effects in molecules. For example, it has recently been possible [15] to recover approximately 84% of the correlation energy of the nitrogen molecule at its equilibrium nuclear geometry using third-order many-body perturbation theory together with a universal even-tempered basis set. It is probable that basis set truncation is the largest source of error in this and similar calculations. In this paper calculations are reported for the ground state of the beryllium atom and the neon atom using the systematic sequence of basis sets given by Schmidt and Ruedenberg [10]. The purpose of this work is to examine the convergence properties of the many-body perturbation series with respect to basis set size for these two atoms. We include only functions of symmetries which arise at the Hartree–Fock level in these prototypical calculations.

2. Systematic Sequences of Even-Tempered Gaussian Primitives

The concept of an even-tempered basis set has been shown to be useful in atomic and molecular calculations both at the Hartree–Fock level [3–11, 13, 14] and including correlation effects [12, 15]. In an even-tempered basis set the orbital exponents are given by a geometric series

$$\zeta_k = \alpha_l \beta_l^k; \qquad k = 1, 2, \ldots, N_l \tag{1}$$

where l denotes the symmetry type of a particular set of orbitals. The elements of the overlap matrix then obey the relationship

$$\Delta_{i,j} = \Delta_{i+1,j+1}; \qquad \forall i, j \tag{2}$$

For an even-tempered basis set to approach a complete set as the value of N_l is increased the values of α_l and β_l must be functions of N_l. Since

$$\alpha_l \to 0 \qquad \beta_l \to 1 \qquad \beta_l^{N_l} \to \infty \tag{3a}$$

as

$$N_l \to \infty \tag{3b}$$

Ruedenberg and coworkers [9, 10] have suggested that the empirical forms

$$\ln \ln \beta_l = b_l \ln N_l + b'_l \tag{4}$$

and

$$\ln \alpha_l = a_l \ln (\beta_l - 1) + a'_l \tag{5}$$

are useful and have demonstrated this at the Hartree–Fock level for a series of atoms. In this work we take the values of the constants a_l, a'_l, b_l, b'_l from the work of Schmidt and Ruedenberg [10] and perform calculations of the correlation energy using diagrammatic perturbation theory for the beryllium atom and the neon atom. For beryllium the basis set is restricted to functions with s symmetry while for neon the basis set is restricted to s and p functions. Thus the convergence to the "s limit" is examined for Be and convergence to the "sp limit" for Ne. The basis sets used for the beryllium atom will be denoted by $[ns]$. The basis sets employed for the neon atom consisted of $2n$ functions of s symmetry and n functions of p symmetry. They are denoted by $[2ns/np]$. These basis sets have been termed *energy balanced* by Schmidt and Ruedenberg [10]. For beryllium $[ns]$, $n = 6, 8, \ldots, 20$ basis sets were used while for neon $[2ns/np]$, $n = 3, 4, \ldots, 9$ were used.

3. Many-Body Perturbation Theory

The many-body perturbation theory approach to electron correlation energies in molecules has been described in detail previously [16] and the purpose of the present section is merely to introduce notation.

Two different zero-order Hamiltonian operators are used in the present study: the matrix Hartree–Fock model Hamiltonian and the shifted Hamiltonian [16]. Quantities derived from the latter Hamiltonian will be distinguished by a tilde. From third-order calculations we can form $[N/M]$ Padé approximants, $N + M = 3$ and we denote the energies corresponding to these by $E[N/M]$. The [2/1] Padé approximants to the perturbation series are of particular interest because of their invariance properties [17]. Finally, we denote by E(var) the variational upper bound obtained by substituting the first-order wave function $\Phi_0 + \lambda\Phi_1$ in the Rayleigh quotient and treating λ as a variational parameter.

4. Computational Details

The computations described in this work were performed on the IBM 370/165 computer at the S.R.C. Daresbury Laboratory.

The integrals over Gaussian primitive functions, self-consistent-field and transformation phases of the calculation were performed by using the ATMOL3 suite of programs [18]. The self-consistent-field iterations were continued until no off-diagonal element of the Fock matrix in the molecular orbital basis had a magnitude greater than 10^{-5}. (Increasing this accuracy parameter to 10^{-9} produced changes of less than 10^{-7} in all of the energies calculated for the beryllium atom using the [6*s*] basis set and the [20*s*] basis set.) The correlation calculations were done with the diagrammatic many-body perturbation theory programs of Silver [19, 20] and the present author [21].

5. Results and Discussion

The results of the calculations on the beryllium atom are presented in Table 1 and those for the neon atom are given in Table 2. For both the beryllium atom and the neon atom the self-consistent field energies are, of course, in exact agreement with those given by Schmidt and Ruedenberg [10]. For all of the energy quantities given in Table 1 for the beryllium atom there is a change of less than 20 microhartrees on passing from the [18*s*] to the [20*s*] basis set. For the neon atom the energy quantities given in Table 2 change by less than 1.5 millihartrees on passing from the [16*s*/8*p*] to the [18*s*/9*p*] basis set. The energy quantities given in Tables 1 and 2 are seen to decrease monotonically as the size of the basis set is increased except for $\tilde{E}[3/0]$ and $\tilde{E}[2/1]$ for the Be atom. Note that if $S(N)$ denotes the n-electron space which may be generated from a one-electron basis set consisting of N functions then, if Eqs. (1), (4) and (5) are used to define basis sets, in general $S(N) \not\subset S(N+1)$ and therefore the energy corresponding to $S(N+1)$ is not necessarily lower than that corresponding to $S(N)$. For the beryllium atom using the [20*s*] basis set the differences $|E[3/0]-E[2/1]| = {\sim}0.3$ mH (millihartree) and $|\tilde{E}[3/0]-\tilde{E}[2/1]| = {\sim}0.1$ mH, suggest that the perturbation expansion with shifted denominators is the more rapidly convergent of the two series considered in this work. The differences $|E[3/0]-\tilde{E}[3/0]| = {\sim}0.5$ mH and $|E[2/1]-\tilde{E}[2/1]| = {\sim}0.2$ mH suggest that the [2/1] Padé approximants are a more appropriate representation of the energy than the [3/0] Padé approximants. For the neon atom, using the [18*s*/9*p*] basis set the differences $|E[3/0]-E[2/1]| = {\sim}0.1$ MH, $|\tilde{E}[3/0]-\tilde{E}[2/1]| = {\sim}4.6$ mH, $|E[3/0]-\tilde{E}[3/0]| = {\sim}5.7$ mH and $|E[2/1]-\tilde{E}[2/1]| = {\sim}1.2$ mH suggest that the [2/1] Padé approximant constructed from the perturbation series corresponding to the Hartree–Fock model is to be preferred. The convergence properties of the model and shifted perturbation series have been considered in some detail previously for the Be and Ne atoms [22].

Following Schmidt and Ruedenberg [10] we used the Hartree extrapolation technique to estimate the basis set limit of the various energy values. Thus we define the quantity

$$E_{\infty}(N) = (E(N)E(N-2) - E(N-1)^2)/(E(N) - 2E(N-1) + E(N-2)) \qquad (6)$$

where $E(N)$ denotes the energy corresponding to a particular basis set, $E(N-1)$ and $E(N-2)$ the energies corresponding to the next two smaller basis sets. This

Table 1. Diagrammatic many-body perturbation theory calculations for the beryllium atom using the regularised basis sets of Schmidt and Ruedenberg[a]

Basis set	E(SCF)	$E[3/0]$	$E[2/1]$	E(var)	$\tilde{E}[3/0]$	$\tilde{E}[2/1]$	$\tilde{E}$(var)
6*s*	−14.53489699	−14.551789	−14.552037	−14.552010	−14.552111	−14.552118	−14.552084
8*s*	−14.56644167	−14.584205	−14.584530	−14.584484	−14.584751	−14.584766	−14.584690
10*s*	−14.57172696	−14.589711	−14.590049	−14.589997	−14.590275	−14.590304	−14.590217
12*s*	−14.57270546	−14.590749	−14.591090	−14.591037	−14.591286	−14.591334	−14.591250
14*s*	−14.57295146	−14.591029	−14.591372	−14.591319	−14.591547	−14.591612	−14.591532
16*s*	−14.57300182	−14.591092	−14.591436	−14.591383	−14.591589	−14.591669	−14.591590
18*s*	−14.57301682	−14.591113	−14.591457	−14.591404	−14.591588	−14.591681	−14.591604
20*s*	−14.57302132	−14.591121	−14.591465	−14.591412	−14.591574	−14.591680	−14.591604

[a] All energies are in Hartree atomic units

Table 2. Diagrammatic many-body perturbation theory calculations for the neon atom using the regularised even-tempered basis set of Schmidt and Ruedenberg[a]

Basis set	E(SCF)	$E[3/0]$	$E[2/1]$	E(var)	$\tilde{E}[3/0]$	$\tilde{E}[2/1]$	$\tilde{E}$(var)
6*s*/3*p*	−128.07977275	−128.221544	−128.221548	−128.219644	−128.214882	−128.220611	−128.218586
8*s*/4*p*	−128.43917164	−128.606675	−128.606726	−128.603621	−128.597036	−128.604984	−128.601602
10*s*/5*p*	−128.51933009	−128.699699	−128.699776	−128.696087	−128.690678	−128.697923	−128.693928
12*s*/6*p*	−128.53935898	−128.724351	−128.724439	−128.720540	−128.716506	−128.722827	−128.718659
14*s*/7*p*	−128.54474484	−128.731220	−128.731314	−128.727345	−128.724270	−128.729889	−128.725687
16*s*/8*p*	−128.54630183	−128.733372	−128.733468	−128.729472	−128.727111	−128.732162	−128.727961
18*s*/9*p*	−128.54681646	−128.734150	−128.734247	−128.730240	−128.728454	−128.733035	−128.728844

[a] All energies are in Hartree atomic units

Table 3. Empirical upper bounds and lower bounds for the beryllium atom[a]

Basis set	E(SCF)	$E[3/0]$	$E[2/1]$	E(var)	$\tilde{E}[3/0]$	$\tilde{E}[2/1]$	$\tilde{E}$(var)
(a) Empirical upper bounds							
10*s*	−14.572791	−14.590838	−14.591179	−14.591125	−14.591401	−14.591435	−14.591345
12*s*	−14.572928	−14.590990	−14.591331	−14.591278	−14.591513	−14.591569	−14.591488
14*s*	−14.573034	−14.591133	−14.591478	−14.591425	−14.591639	−14.591715	−14.591637
16*s*	−14.573015	−14.591111	−14.591455	−14.591401	−14.591597	−14.591683	−14.591606
18*s*	−14.573023	−14.591124	−14.591468	−14.591415	−14.591588	−14.591684	−14.591608
20*s*	−14.573023	−14.591126	−14.591470	−14.591416	−14.591590	−14.591680	−14.591604
(b) Empirical lower bounds							
10*s*	−14.573855	−14.591964	−14.592308	−14.592253	−14.592527	−14.592567	−14.592474
12*s*	−14.573150	−14.591231	−14.591573	−14.591520	−14.591739	−14.591804	−14.591725
14*s*	−14.573117	−14.591236	−14.591583	−14.591530	−14.591730	−14.591818	−14.591742
16*s*	−14.573028	−14.591129	−14.591473	−14.591420	−14.591605	−14.591698	−14.591621
18*s*	−14.573030	−14.591134	−14.591478	−14.591425	−14.591588	−14.591687	−14.591612
20*s*	−14.573025	−14.591130	−14.591474	−14.591421	−14.591605	−14.591680	−14.591604
(c) Average value							
10*s*	−14.573323	−14.591401	−14.591743	−14.591689	−14.591964	−14.592001	−14.591909
12*s*	−14.573039	−14.591111	−14.591452	−14.591399	−14.591626	−14.591687	−14.591607
14*s*	−14.573075	−14.591184	−14.591531	−14.591477	−14.591684	−14.591766	−14.591690
16*s*	−14.573021	−14.591120	−14.591464	−14.591411	−14.591601	−14.591690	−14.591614
18*s*	−14.573026	−14.591129	−14.591473	−14.591420	−14.591588	−14.591686	−14.591610
20*s*	−14.573024	−14.591128	−14.591472	−14.591419	−14.591597	−14.591680	−14.591604
(d) Deviation							
10*s*	0.000532	0.000563	0.000565	0.000564	0.000563	0.000566	0.000564
12*s*	0.000111	0.000121	0.000121	0.000121	0.000113	0.000118	0.000119
14*s*	0.000041	0.000052	0.000053	0.000053	0.000046	0.000051	0.000053
16*s*	0.000006	0.000009	0.000009	0.000009	0.000004	0.000007	0.000008
18*s*	0.000003	0.000005	0.000005	0.000005	0.000000	0.000001	0.000002
20*s*	0.000001	0.000002	0.000002	0.000002	0.000008	0.000000	0.000000

[a] All energies are in Hartree atomic units

Table 4. Empirical upper bounds and lower bounds for the neon atom[a]

Basis set	E(SCF)	$E[3/0]$	$E[2/1]$	E(var)	$\tilde{E}[3/0]$	$\tilde{E}[2/1]$	$\tilde{E}$(var)
(a) Empirical upper bounds							
10*s*/5*p*	−128.542358	−128.729323	−128.729415	−128.725417	−128.721071	−128.727563	−128.723251
12*s*/6*p*	−128.546031	−128.733240	−128.733333	−128.729332	−128.726343	−128.731943	−128.727708
14*s*/7*p*	−128.546726	−128.733873	−128.733972	−128.729970	−128.727607	−128.732683	−128.728477
16*s*/8*p*	−128.546935	−128.734353	−128.734451	−128.730440	−128.728750	−128.733241	−128.729049
18*s*/9*p*	−128.547071	−128.734591	−128.734688	−128.730672	−128.729661	−128.733580	−128.729405
(b) Empirical lower bounds							
10*s*/5*p*	−128.565387	−128.758946	−128.759054	−128.754747	−128.751465	−128.757202	−128.752574
12*s*/6*p*	−128.552702	−128.742128	−128.742228	−128.738124	−128.736181	−128.741060	−128.736756
14*s*/7*p*	−128.548707	−128.736527	−128.736629	−128.732594	−128.730944	−128.735478	−128.731267
16*s*/8*p*	−128.547568	−128.735335	−128.735433	−128.731407	−128.730389	−128.734321	−128.730137
18*s*/9*p*	−128.547325	−128.735031	−128.735128	−128.731105	−128.730867	−128.734123	−128.729965
(c) Average value							
10*s*/5*p*	−128.553873	−128.744134	−128.744235	−128.740082	−128.736268	−128.742382	−128.737912
12*s*/6*p*	−128.549366	−128.737684	−128.737781	−128.733728	−128.731262	−128.736501	−128.732232
14*s*/7*p*	−128.547716	−128.735200	−128.735301	−128.731282	−128.729275	−128.734081	−128.729872
16*s*/8*p*	−128.547252	−128.734844	−128.734942	−128.730923	−128.729569	−128.733781	−128.729593
18*s*/9*p*	−128.547198	−128.734811	−128.734908	−128.730889	−128.730264	−128.733851	−128.729685
(d) Deviation							
10*s*/5*p*	0.011514	0.014819	0.014819	0.014665	0.015197	0.014820	0.014662
12*s*/6*p*	0.003336	0.004444	0.004447	0.004396	0.004919	0.004558	0.004524
14*s*/7*p*	0.000990	0.001327	0.001329	0.001312	0.001668	0.001397	0.001395
16*s*/8*p*	0.000317	0.000491	0.000491	0.000484	0.000819	0.000540	0.000544
18*s*/9*p*	0.000127	0.000220	0.000220	0.000216	0.000603	0.000272	0.000280

[a] All energies are in Hartree atomic units.

expression provides an empirical upper bound to the basis set limit. The expression

$$\hat{E}_\infty(N) = E_\infty(N) - [E(N) - E_\infty(N)] \tag{7}$$

is an empirical lower bound to the basis set limit. The average of these two values

$$E_{\mathrm{Av}}(N) = (E_\infty(N) + \hat{E}_\infty(N))/2 \tag{8}$$

may be regarded as a "best" estimate of the basis set limit and the quantity

$$D_\infty(N) = (E_\infty(N) - \hat{E}_\infty(N))/2 \tag{9}$$

is an estimate of the accuracy of the "best" value. In Table 3 we give values of the empirical upper bounds, empirical lower bounds, averaged values and deviations for each of the energy values calculated for the Be atom. The corresponding results for the neon atom are displayed in Table 4. It can be seen that the values of $D_\infty(N)$ are smaller for the matrix Hartree–Fock energies than the correlation energies. The correlation energy is more sensitive to the degree of completeness of the basis set than is the matrix Hartree–Fock energy.

6. Concluding Remarks

In this paper, we have shown by means of prototypical calculations on the beryllium atom and the neon atom that the use of systematic sequences of basis sets can prove useful in calculations including electron correlation effects. The approach offers a tractable solution to the basis set truncation problem which seems to be the largest source of error in most accurate calculations on small molecules.

We note that the use of systematic sequences of even-tempered basis sets could be employed in calculations using universal basis sets [11–15]. A given sequence of universal even-tempered basis sets could then be employed for all atoms of the first-row of the periodic table and probably the second row also.

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