

## Stability of the Restricted Hartree-Fock-Roothaan Method

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(Received 19 March 1973)

Newly computed Hartree-Fock-Roothaan wave functions are reported for the atomic negative ions,  $B^-$ ,  $C^{--}$ ,  $N^{--}$ ,  $O^{--}$ ,  $Si^{--}$ ,  $P^{--}$ ,  $S^{--}$ . They are obtained as self-consistently convergent solutions. The implication with regard to the stability of the restricted Hartree-Fock-Roothaan method is also discussed.

### I. INTRODUCTION

The Hartree-Fock approximation is well accepted in physics and chemistry. Sometimes it is taken as something more than a mere approximation that is numerically feasible. It has become a model world in which we tend to see some meaningful reflections of phenomena that would occur in the real physical world. The concept of an electronic phase transition suggested by Mott<sup>1</sup> some 20 years ago may be regarded as one of the earlier examples of this sort.

A more recent example is the paper by Kaplan and Kleiner.<sup>2</sup> Their argument is based on the use of a single Slater-determinantal wave function and a theorem is proved to the effect that in Hartree-Fock theory an electron may always be added to an  $N$ -electron system without raising the energy. The theorem is applied to show that the conventional Hartree-Fock wave function is unstable for certain negative atomic ions (including  $B^-$ ,  $N^{--}$ ,  $O^{--}$ ), and that the typical extent of the instability is chemically significant.

The purpose of the present paper is not to discuss directly the points raised by Kaplan and Kleiner<sup>2</sup> or by Prat,<sup>3</sup> who used an unsatisfactory Hartree-Fock wave function of  $O^{--}$  as a computational starting point. Instead, a set of new numerical results from the restricted Hartree-Fock-Roothaan calculations on negative atomic ions is presented in the hope that it may have some relevance to the subject matter or that it may be of some use numerically. Among these results are the Hartree-Fock-Roothaan wave functions for  $B^-$ ,  $C^{--}$ ,  $N^{--}$ , and  $O^{--}$ , which are much lower in total energy than the ones reported earlier<sup>4</sup> and cited by Kaplan and Kleiner<sup>2</sup> and also by Prat.<sup>3</sup>

A precise definition of what we call here the restricted Hartree-Fock-Roothaan method is in order. The total wave function is, in general, a linear combination of several Slater determinants each of which contains (doubly occupied) closed-shell cores  $\{\psi_k\}$  and open shells  $\{\psi_n\}$ . The coefficients of the linear combination of the determinants are determined by the requirement that the

total wave function be a proper eigenfunction of both  $S^2$  and  $S_z$  spin operators. In Roothaan's expansion method, the orbital  $\psi_i$ , or, to be more precise,  $\psi_{i\lambda\alpha}$  is expanded in terms of symmetry basis functions  $x_{p\lambda\alpha}$ :

$$\psi_{i\lambda\alpha} = \sum_p x_{p\lambda\alpha} C_{\lambda p i},$$

where  $\lambda$  refers to the irreducible representation or symmetry species and  $\alpha$  refers to the subspecies. In a simple atomic example,  $\lambda$  stands for  $l$  and  $\alpha$  for  $m_l$  in the common notation. The Hartree-Fock-Roothaan equation determines the coefficients  $\{C_{\lambda p i}\}$ . It is important to remind ourselves that the coefficients do not depend on  $\alpha$ . The implications are that in an atomic calculation we will obtain, inevitably, a set of symmetry orbitals and that the radial functions are identical for all subspecies belonging to a particular symmetry. These restrictions are sometimes referred to as the symmetry restriction and the equivalence restriction, respectively.

In Sec. II we report some newly obtained restricted Hartree-Fock-Roothaan solutions for several negative ions. In Sec. III, an attempt to drop the equivalence restriction in the case of the  $^3P$ ,  $^1D$ , and  $^1S$  states of  $B^-$  will be described.

### II. NEGATIVE ATOMIC IONS

Not infrequently it occurs that an attempt to obtain a Hartree-Fock solution is plagued by non-convergence. Such is the case for the restricted Hartree-Fock-Roothaan solutions of  $B^-(^1S)$ ,  $N^{--}(^2P)$ , and  $O^{--}(^1S)$  as mentioned by Kaplan and Kleiner.<sup>2</sup> In Tables I-III the solutions of  $C^{--}(^3P)$ ,  $N^{--}(^2P)$ , and  $O^{--}(^1S)$  are given which have appreciably lower total energies than the ones hitherto reported.<sup>4</sup> Also given in Tables IV-VI are the solutions of  $Si^{--}(^3P)$ ,  $P^{--}(^2P)$ , and  $S^{--}(^1S)$ . In these tables the total energy and the orbital energies are given in atomic units and the abbreviation such as STO ( $5s$ ,  $4p$ ) implies that  $5s$ -type  $4p$ -type Slater-type orbitals are used as the basis functions. The first column under the heading or-

TABLE I.  $C^{-} 1s(2)2s(2)2p(4)^3P$  STO (5s, 4p). Total energy =  $-0.374\ 843\ 57\ 10(2)$ .

Orbital symmetry Energy exponent	1s	2s
	-0.110 679 25 10(2)	-0.425 753 54 10(0)
1s 0.918 565 07 10(1)	0.950 545 00 10(-1)	0.207 383 73 10(-2)
1s 0.526 700 90 10(1)	0.926 507 75 10(0)	-0.245 514 95 10(0)
3s 0.631 618 60 10(1)	-0.182 100 00 10(-1)	-0.339 816 93 10(-1)
2s 0.198 177 27 10(1)	0.272 709 47 10(-2)	0.678 319 33 10(0)
2s 0.114 240 69 10(1)	-0.464 456 83 10(-3)	0.417 540 59 10(0)
Orbital symmetry Energy exponent	2p	
	0.375 367 01 10(-1)	
2p 0.521 449 98 10(1)	0.202 628 37 10(-1)	
2p 0.193 942 85 10(1)	0.384 285 61 10(0)	
2p 0.781 040 46 10(0)	0.517 191 53 10(0)	
2p 0.988 639 61 10(-1)	0.521 265 31 10(0)	

Orbital indicates the individual characteristics. To be more precise, the basis functions are primitive Slater-type orbitals,

$$\psi = \sum C_i x(n_i, l_i, m_i; \xi_i),$$

$$x(n, l, m; \xi) = [(2n)!]^{-1/2} (2\xi)^{n+1/2} r^{n-1} e^{-\xi r} Y_{lm}(\theta, \phi).$$

It is to be noted that  $C_i$  do not depend on the quantum number  $m$ . The atomic self-consistent-field program in use has been carefully coded so as to be free as much as possible from instabilities which could be removed by proper numerical precautions. Under careful input preparation and parameter variation, the program functions in an orderly way in most circumstances but it is not claimed that the present solutions are the best obtainable within the framework of the present approximation.

It must be clearly understood that the instability we are referring to here is the one which we en-

TABLE II.  $N^{-} 1s(2)2s(2)2p(5)^2P$  STO (5s, 4p). Total energy =  $-0.540\ 620\ 11\ 10(2)$ .

Orbital symmetry Energy exponent	1s	2s
	-0.152 600 36 10(2)	-0.550 441 56 10(0)
1s 0.105 736 24 10(2)	0.962 356 99 10(-1)	0.443 146 92 10(-2)
1s 0.618 720 35 10(1)	0.926 767 42 10(0)	-0.257 457 93 10(0)
3s 0.751 051 90 10(1)	-0.209 724 88 10(-1)	-0.308 407 74 10(-1)
2s 0.238 190 56 10(1)	0.302 591 92 10(-2)	0.680 303 88 10(0)
2s 0.134 058 10 10(1)	-0.332 621 33 10(-3)	0.421 059 10 10(0)
Orbital symmetry Energy exponent	2p	
	0.531 776 64 10(-1)	
2p 0.651 366 75 10(1)	0.196 749 38 10(-1)	
2p 0.244 153 99 10(1)	0.417 042 45 10(0)	
2p 0.985 264 27 10(0)	0.543 373 83 10(0)	
2p 0.137 763 94 10(0)	0.424 430 46 10(0)	

TABLE III.  $O^{-} 1s(2)2s(2)2p(6)^1S$  STO (5s, 4p). Total energy =  $-0.745\ 071\ 27\ 10(2)$ .

Orbital symmetry Energy exponent	1s	2s
	-0.201 262 68 10(2)	-0.704 452 59 10(0)
1s 0.127 577 21 10(2)	0.779 085 83 10(-1)	0.417 543 63 10(-2)
1s 0.709 330 82 10(1)	0.954 842 41 10(0)	-0.263 500 17 10(0)
3s 0.897 081 41 10(1)	-0.335 775 30 10(-1)	-0.265 078 68 10(-1)
2s 0.275 360 19 10(1)	0.280 791 41 10(-2)	0.693 431 47 10(0)
2s 0.152 665 49 10(1)	-0.109 128 17 10(-3)	0.409 036 05 10(0)
Orbital symmetry Energy exponent	2p	
	0.656 964 39 10(-1)	
2p 0.499 579 54 10(1)	0.847 542 97 10(-1)	
2p 0.244 937 82 10(1)	0.481 274 30 10(0)	
2p 0.104 211 45 10(1)	0.467 025 01 10(0)	
2p 0.165 196 58 10(0)	0.341 915 69 10(0)	

counter within the so-called symmetry and equivalence restrictions. The solutions always remain within the limits of these restrictions. Physically speaking these atomic ions would certainly not exist as free entities, but still it is interesting to observe that the restricted Hartree-Fock-Roothaan equations yield solutions for them which are self-consistently convergent within the framework of the expansion method. In reality, one outermost electron will move away to infinite distance but in the strange world of the restricted Hartree-Fock-Roothaan approximation all the electrons in the  $p$  shell are forced to stay together on an equal footing because the identical radial functions are assigned to them by the very setup of the approximation. This is reflected in the fact that in all cases reported in the present section the highest orbital energy is positive and very close to zero.

### III. $^3P$ , $^1D$ , AND $^1S$ STATES OF $B^{-}$

A convergence difficulty has been reported in the Hartree-Fock-Roothaan calculation of the  $^1S$  state of  $B^{-}$ .<sup>4</sup> In the present calculation we have overcome this numerical difficulty and obtained a new set of the wave functions for  $^3P$ ,  $^1D$ , and  $^1S$  states of  $B^{-}$ , but the  $2p$  orbital energy of the  $^1S$  state remains slightly positive (+0.002164 a.u.). The  $(^1S-^1D)/(^1D-^3P)$  ratio turns out to be 1.209 while the "experimental" value is estimated to be about 1.10 by extrapolation from the isoelectronic sequence. The numerical data of the Hartree-Fock-Roothaan wave functions are given in Table VII.

The next step we have taken is the relaxation of the equivalence restriction on the  $p$ -shell orbitals. There is a wide range of possibility of splitting the  $p$  shell. We have made the following simple choice: For brevity, we shall write down only

TABLE IV.  $\text{Si}^{--} 1s(2)2s(2)2p(6)3s(2)3p(4)^3P$  STO (8s, 8p). Total energy =  $-0.288\ 738\ 19\ 10(3)$ .

Orbital symmetry	1s	2s	3s
Energy	-0.685 995 48 10(2)	-0.594 027 68 10(1)	-0.321 174 80 10(0)
exponent			
1s 0.140 000 00 10(2)	0.969 210 36 10(0)	-0.257 931 84 10(0)	0.647 183 78 10(-1)
3s 0.156 854 03 10(2)	0.346 182 92 10(-1)	-0.113 034 94 10(-3)	0.171 246 15 10(-2)
3s 0.966 728 92 10(1)	0.302 457 11 10(-1)	0.202 168 20 10(0)	-0.100 553 10 10(0)
3s 0.873 651 51 10(1)	-0.194 692 60 10(-1)	0.100 579 86 10(0)	0.370 767 12 10(-1)
3s 0.601 198 19 10(1)	0.240 309 22 10(-2)	0.577 422 28 10(0)	-0.208 319 02 10(0)
3s 0.429 101 27 10(1)	-0.208 757 50 10(-3)	0.207 433 28 10(0)	-0.588 281 78 10(-1)
3s 0.192 710 99 10(1)	-0.776 546 40 10(-5)	0.307 965 46 10(-3)	0.729 357 14 10(0)
3s 0.110 363 79 10(1)	-0.372 831 87 10(-6)	0.299 002 35 10(-3)	0.378 253 05 10(0)
Orbital symmetry	2p	3p	
Energy	-0.404 052 96 10(1)	0.256 099 12 10(-1)	
exponent			
2p 0.700 000 00 10(1)	0.568 291 65 10(0)	-0.839 437 63 10(-1)	
4p 0.114 484 83 10(2)	0.230 478 92 10(-1)	-0.307 406 78 10(-2)	
4p 0.712 694 73 10(1)	0.270 777 02 10(0)	-0.373 284 14 10(-1)	
4p 0.487 436 58 10(1)	0.262 550 65 10(0)	-0.179 095 08 10(-1)	
4p 0.255 289 44 10(1)	0.122 089 37 10(-1)	0.251 707 46 10(0)	
4p 0.141 411 08 10(1)	-0.147 104 07 10(-2)	0.472 033 59 10(0)	
4p 0.673 708 03 10(0)	0.487 874 22 10(-3)	0.323 132 43 10(0)	
4p 0.119 281 61 10(0)	0.961 735 41 10(-4)	0.496 538 24 10(0)	

the relevant  $p$ -electron part of the total wave function:

$$({}^3P): \{[p_+(1)p'_0(2) - p'_0(1)p_+(2)] + [p'_+(1)p_0(2) - p_0(1)p'_+(2)]\} \alpha(1)\alpha(2),$$

$$({}^1D): [p_+(1)p'_+(2) + p'_+(1)p_+(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)],$$

$$({}^1S): \{[p_+(1)p'_-(2) + p'_-(1)p_+(2)] + [p_-(1)p'_+(2) + p'_+(1)p_-(2)] - [p_0(1)p'_0(2) + p'_0(1)p_0(2)]\} [\alpha(1)\beta(2) - \beta(1)\alpha(2)].$$

TABLE V.  $\text{P}^{--} 1s(2)2s(2)2p(6)3s(2)3p(5)^2P$  STO (8s, 8p). Total energy =  $-0.340\ 534\ 55\ 10(3)$ .

Orbital symmetry	1s	2s	3s
Energy	-0.796 696 65 10(2)	-0.720 590 76 10(1)	-0.392 759 05 10(0)
exponent			
1s 0.150 000 00 10(2)	0.970 787 06 10(0)	-0.263 575 27 10(0)	0.706 351 90 10(-1)
3s 0.167 858 64 10(2)	0.326 452 63 10(-1)	0.266 613 83 10(-3)	0.206 997 15 10(-2)
3s 0.105 986 80 10(2)	0.216 378 42 10(-1)	0.175 915 42 10(0)	-0.870 100 80 10(-1)
3s 0.903 353 62 10(1)	-0.111 444 69 10(-1)	0.172 295 30 10(0)	0.127 058 95 10(-1)
3s 0.627 677 70 10(1)	0.244 057 96 10(-2)	0.614 804 98 10(0)	-0.261 277 72 10(0)
3s 0.438 805 38 10(1)	-0.369 063 78 10(-3)	0.123 294 42 10(0)	-0.154 642 67 10(-1)
3s 0.216 787 53 10(1)	0.120 730 51 10(-4)	-0.651 092 94 10(-3)	0.759 071 60 10(0)
3s 0.122 542 83 10(1)	-0.904 554 43 10(-5)	0.664 366 38 10(-3)	0.351 413 42 10(0)
Orbital symmetry	2p	3p	
Energy	-0.509 690 72 10(1)	0.347 094 80 10(-1)	
exponent			
2p 0.750 000 00 10(1)	0.592 300 14 10(0)	-0.108 148 02 10(0)	
4p 0.124 267 39 10(2)	0.200 855 98 10(-1)	-0.322 287 98 10(-2)	
4p 0.775 903 60 10(1)	0.252 059 25 10(0)	-0.426 280 47 10(-1)	
4p 0.542 729 59 10(1)	0.250 341 91 10(0)	-0.206 110 02 10(-1)	
4p 0.295 120 91 10(1)	0.119 592 75 10(-1)	0.294 228 38 10(0)	
4p 0.166 690 12 10(1)	-0.924 158 55 10(-3)	0.496 711 88 10(0)	
4p 0.809 450 07 10(0)	0.567 274 62 10(-3)	0.313 903 43 10(0)	
4p 0.154 847 91 10(0)	0.266 361 54 10(-3)	0.390 808 62 10(0)	

TABLE VI.  $S^{2-} 1s(2)2s(2)2p(6)3s(2)3p(6) {}^1S$  STO (8s, 8p). Total energy = -0.397 368 37 10(3).

Orbital symmetry	1s	2s	3s
Energy exponent	-0.915 764 51 10(2)	-0.857 215 50 10(1)	-0.466 617 66 10(0)
1s	0.160 000 00 10(2)	0.972 206 81 10(0)	-0.268 511 21 10(0)
3s	0.177 524 72 10(2)	0.321 215 82 10(-1)	0.170 817 25 10(-2)
3s	0.107 453 76 10(2)	0.331 600 23 10(-1)	0.356 340 96 10(0)
3s	0.994 350 32 10(1)	-0.241 025 22 10(-1)	-0.587 587 06 10(-1)
3s	0.695 770 90 10(1)	0.208 583 53 10(-2)	0.649 417 50 10(0)
3s	0.486 720 98 10(1)	-0.153 826 52 10(-3)	0.136 017 21 10(0)
3s	0.240 648 09 10(1)	-0.399 005 81 10(-4)	0.273 089 24 10(-3)
3s	0.134 643 08 10(1)	0.347 411 07 10(-5)	0.608 364 42 10(-3)
Orbital symmetry	2p	3p	
Energy exponent	-0.625 214 80 10(1)	0.483 621 68 10(-1)	
2p	0.800 000 00 10(1)	0.613 852 57 10(0)	-0.127 119 01 10(0)
4p	0.127 934 12 10(2)	0.232 141 44 10(-1)	-0.573 149 53 10(-2)
4p	0.820 141 16 10(1)	0.249 723 42 10(0)	-0.392 449 47 10(-1)
4p	0.590 101 62 10(1)	0.218 879 47 10(0)	-0.393 750 60 10(-1)
4p	0.357 711 67 10(1)	0.119 329 72 10(-1)	0.281 053 97 10(0)
4p	0.201 819 92 10(1)	-0.331 122 68 10(-3)	0.535 410 12 10(0)
4p	0.979 827 55 10(0)	0.141 016 87 10(-3)	0.332 108 55 10(0)
4p	0.211 002 66 10(0)	-0.768 777 04 10(-5)	0.303 101 20 10(0)

In the above wave functions we have two different radial functions indicated by "no prime" and "prime" on the  $p$ 's. The Hartree-Fock (1s) and (2s) orbitals given in Table VII are used for the  $s$ -electron core part of the total wave functions. For  $p$  and  $p'$  we have tried the following two simple ideas.

#### A. Primitive Slater-Type Orbitals

We first use the primitive Slater-type  $p$  orbitals with separate exponent parameters  $\xi$  and  $\xi'$ ,

$$p \sim r e^{-\xi r}, \quad p' \sim r e^{-\xi' r}.$$

For the ground  ${}^3P$  state we find a split-shell solution as follows:

$$\xi = 1.3172, \quad \xi' = 0.5185 \quad E({}^3P) = -24.51342 \text{ a.u.}$$

This compares well with the value -24.47375 a.u. ( $\xi = \xi' = 0.9536$ ). This solution is stable in the mathematical sense that the above set of  $\xi$  and  $\xi'$  gives a deep minimum point in the total energy. However, for both  ${}^1D$  and  ${}^1S$  states the split-shell wave functions turn out to be unstable: The energies continue to get lower as the smaller exponent  $\xi'$  tends to zero; that is to say, the system tends to release one electron. This is not an entirely unexpected phenomenon.

#### B. Scaled Hartree-Fock-Roothaan Orbitals

We shall apply a special kind of scaling to the Hartree-Fock-Roothaan orbitals. The idea was

TABLE VII.  $B^- ({}^3P, {}^1D, {}^1S)$ .

	${}^3P$	${}^1D$	${}^1S$
$E^a$	-24.519 18	-24.490 55	-24.455 94
$\xi(1s)$	6.773 559	6.786 171	6.859 483
(1s)	3.472 672	3.503 796	3.570 754
(3s)	4.414 845	4.429 423	4.479 793
(2s)	1.639 735	1.639 874	1.644 566
(2s)	0.903 310	0.926 276	0.975 397
$\xi(2p)$	4.872 166	4.502 706	3.552 350
(2p)	1.823 264	1.695 529	1.436 116
(2p)	0.901 477	0.787 265	0.584 709
(2p)	0.415 181	0.306 307	0.156 195
$\epsilon^b(1s)$	-7.424 928	-7.471 860	-7.555 665
$C(1s)$	0.275 284	0.270 394	0.254 020
	0.860 216	0.859 975	0.868 237
	-0.156 448	-0.150 375	-0.140 495
	-0.002 873	-0.002 563	-0.002 408
	0.001 022	0.000 949	0.000 948
$\epsilon^b(2s)$	-0.242 480	-0.276 009	-0.341 738
$C(2s)$	-0.027 615	-0.027 015	-0.024 865
	-0.232 105	-0.236 132	-0.242 158
	-0.001 753	-0.004 291	-0.008 562
	0.603 822	0.619 132	0.627 718
	0.507 496	0.489 895	0.475 979
$\epsilon^b(2p)$	-0.026 360	-0.007 982	0.002 164
$C(2p)$	0.011 304	0.014 114	0.029 663
	0.239 213	0.287 506	0.380 315
	0.542 720	0.542 852	0.521 424
	0.360 819	0.359 199	0.389 232

<sup>a</sup> Total energy in atomic units.

<sup>b</sup> Orbital energies in atomic units.

TABLE VIII. Term energies of B<sup>-</sup> (in atomic units) with scaled Hartree-Fock-Roothaan orbitals.

	$\lambda=\lambda'$	$\lambda\neq\lambda'$	$\lambda=\lambda'$	$\lambda$	$\lambda'$
<sup>3</sup> P	-24.519 18	-24.523 01	1.0	1.294 02	0.668 849
<sup>1</sup> D	-24.490 55	-24.496 26	1.0	1.345 42	0.598 314
<sup>1</sup> S	-24.455 94	-24.461 88	1.0	1.374 36	0.578 685

explained in detail elsewhere.<sup>5</sup> The point is that we may insert a scaling parameter into individual Roothaan-type expansions without touching the expansion coefficients  $C_i$ . Thus we define a function generated from the expansion in Sec. II as

$$\psi(\lambda) = \sum_i C_i x(n_i, l_i, m_i; \lambda \xi_i)$$

and regard the original Hartree-Fock-Roothaan orbital as being given by putting  $\lambda = 1.0$ . By the use of the parameter  $\lambda$ , we can contract or expand the original orbital just as we have done with the primitive Slater-type orbital.

In contrast to the case of primitive Slater-type orbitals in Sec. III A we managed to locate a "local" energy minimum on the  $(\lambda, \lambda')$  parameter surface even for the <sup>1</sup>S state, but the minimum region is very shallow around the parameter values given in Table VIII. Beyond  $\lambda' = 0.1$  to smaller values the total energy becomes lower than the local minimum value shown in Table VIII, indicating that the system tends to release one outermost electron. It appears to be difficult to attach any real physical significance to this shallow local minimum. It may be connected with the fact that

we use a rather modest size of STO basis functions, although the size has been known to be large enough to produce a near-Hartree-Fock solution for the ground state of the neutral boron atom.

#### IV. SUMMARY

We have presented some carefully computed Hartree-Fock-Roothaan wave functions for several double-negative free atomic ions. Since the total wave functions are forced to have the symmetry presumed to be characteristic of the ground states by imposing the symmetry and equivalence restrictions on the orbitals, we do not learn much about the instability of the solutions when the restrictions are removed.<sup>3,6</sup> On the other hand, when one tends to regard the Hartree-Fock approximation as a kind of model world, it is interesting to observe that the restricted Hartree-Fock-Roothaan does have at least quasistable solutions for these double-negative atomic ions.

In order to gain an insight into the problem of the instability of the Hartree-Fock-Roothaan solution we have chosen the case of B<sup>-</sup>. We have demonstrated that if one removes the equivalence restriction on the *p*-shell orbitals both <sup>1</sup>D and <sup>1</sup>S solutions become numerically unstable within the Roothaan-expansion approximation employed in the present calculation. However, it would be hazardous to draw any general conclusion about the stability or instability of the various solutions from the results obtained in the present work.

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<sup>3</sup>R. F. Prat, Phys. Rev. A 6, 1735 (1972).

<sup>4</sup>E. Clementi and A. D. McLean, Phys. Rev. 133, A419

(1964).

<sup>5</sup>S. Huzinaga, Theor. Chim. Acta 15, 12 (1969).

<sup>6</sup>Important references may be found in J. Cizek and J. Paldus, J. Chem. Phys. 47, 3976 (1967); J. Paldus and J. Cizek, Chem. Phys. Lett. 3, 1 (1969).