THE WEIGHT FUNCTIONS FOR HE TO AR GAUSSIAN AND SLATER TYPE UNIVERSAL BASIS SETS ORIGINATED BY THE INTEGRAL HARTREE-FOCK METHOD

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ABSTRACT

The Griffin-Hill-Wheeler-Hartree-Fock-(integral Hartree-Fock) method is discussed in the context of generating good quality basis sets for the first two row atoms. Both Gaussian and Slater type basis functions for these atoms are explicitly provided. The role of the behaviour and integration ranges of the weight functions is emphasized.

RESUMO

O método Griffin-Hill-Wheeler-Hartree-Fock (Hartree--Fock integral) é discutido no contexto da geração de conjuntos base de boa qualidade para átomos das primeiras e segundas filas. São fornecidos explicitamente funções de base Gausianas e tipo Slater para estes átomos. O papel do comportamento das funções peso e dos intervalos de integração é enfatizado.

1. INTRODUCTION

Recently we presented universal basis sets for atoms He to Ne and He to Ar for both Gaussian and Slater type functions[1,2]. These sets were obtained through an integral version of the Hartree-Fock (HF) equations[3] which were solved by an integral discretization (ID) technique introduced by one of us[4]. The background for the formulation of the integral HF equations was the Generator Coordinate Method (GCM)[5]. The GCM is characterized by an integral transform trial function

$$\Psi(x) = \int_0^\infty \phi(x,\alpha)\ f(\alpha)\, d\alpha \qquad (1)$$

where $\phi(x,\alpha)$ is the generator function (g.f.), $f(\alpha)$ is an unknown weight function (w.f.), α is the generator coordinate (g.c.) and x denotes space and spin variables. The minimization of the energy expectation value with ansatz (1) leads to the Griffin-Hill-Wheeler (GHW) equation.

In previous works[1-4,6-8] we introduced the use of the ansatz (1) for generating HF atomic orbitals and Universal Gausian and Slater basis sets.

Although those studies gave some attention to the GCM w.f., we wish now to emphasize its role in the context of many electron systems. In Section 2 we provide an outline of the integral HF method. In Section 3 we discuss the behaviour and possible applications of the w.f.'s of the He to Ar Gaussian and Slater type basis sets. Finally, in the Apendix we provide the discretized w.f.'s (expansion coefficents) for our basis sets.

2. THEORY

One can take ansatz (1) as an extended form for the independent particle model

$$\hat{\psi}_i(1) = \int \phi_i(1,\alpha)\, f_i(\alpha)\, d\alpha\,, \quad i = 1, \ldots, n \qquad (2)$$

and build the Slater determinant (ground state, closed shell case)

$$\Psi(1, \ldots, 2n) = |\ \psi_1 \bar{\psi}_1 \ldots \bar{\psi}_n\ (2n)|\,. \qquad (3)$$

By writing the energy expectation value with determinant Ψ and varying respect the w.f.'s f_i one obtains the GHW-HF eqs.[3]

$$\int [F(\alpha,\beta) - \epsilon_i S(\alpha,\beta)]\ f_i(\beta)\, d\beta = 0,\ i = 1, \ldots, n. \qquad (4)$$

In eq. (4) the ϵ_i are the orbital energies and the definition of the Fock and overlap kernels are

$$F(\alpha,\beta) = h(\alpha,\beta) + \sum_j^N [2\, J_j(\alpha,\beta) - K_j(\alpha,\beta)] \qquad (5)$$

and

$$S(\alpha,\beta) = \langle \phi_i(1,\alpha) \mid \phi_i(1,\beta) \rangle\,, \qquad (6)$$

respectvely. The explicit expressions for $h(\alpha,\beta)$ and the Coulomb and exchange kernels are

$$h(\alpha,\beta) = \langle \phi_i(1,\alpha) \mid h(1) \mid \phi_i(1,\beta) \rangle, \qquad (7)$$

$$J_j(\alpha,\beta) = \int\int d\alpha'\, d\beta'\, f_j(\alpha')\, f_j(\beta')\, V(\alpha,\alpha';\beta',\beta) \qquad (8)$$

and

$$K_j(\alpha,\beta) = \int\int d\alpha'\, d\beta'\, f_j(\alpha')\, f_j(\beta')\, V(\alpha,\alpha';\beta,\beta') \quad (9)$$

with

$$V(\alpha,\alpha';\beta',\beta) = \langle \phi_i(1,\alpha)\, \phi_j(2,\alpha')\, |r_{12}^{-1}|\, \phi_j(2,\beta')\, \phi_i(1,\beta) \rangle \quad (10)$$

and

$$V(\alpha,\alpha';\beta,\beta') = \langle \phi_i(1,\alpha)\, \phi_j(2,\alpha')\, |r_{12}^{-1}|\, \phi_i(2,\beta)\, \phi_j(1,\beta') \rangle. \quad (11)$$

All the space integrals are performed analytically and the eqs. (4) are solved through iteration. At each iteration, integrals over the g.c. space are discretized according to

$$\sum_{\ell}^{N} [F(\alpha_k,\beta_\ell) - \epsilon_i S(\alpha_k,\beta_\ell)]\, f_i(\beta_\ell) = 0, \quad (12)$$

where N is the number of discretization points.

The matrix elements $h(\alpha_k,\beta_\ell)$ and $S(\alpha_k,\beta_\ell)$ have obvious definitions and

$$J_j(\alpha_k,\beta_\ell) = \sum_{m}^{N}\sum_{n}^{N} f_i(\alpha'_m)\, f_j(\beta'_n)\, V(\alpha_k,\alpha'_m;\beta'_n,\beta_\ell), \quad (13)$$

$$K_j(\alpha_k,\beta_\ell) = \sum_{m}^{N}\sum_{n}^{N} f_j(\alpha'_m)\, f_j(\beta'_n)\, V(\alpha_k,\alpha'_m;\beta_\ell,\beta'_n). \quad (14)$$

The g.f.'s $\phi(1,\alpha)$ are Gaussian or Slater type orbitals (GTO's, STO's). In the case of GTO's the w.f.'s decrease very slowly with increasing values of the g.c. α. To narrow the w.f.'s we resorted to a relabeling techinique of the g.c. space[4], i.e.,

$$\Omega = \frac{\log \alpha}{A}, \quad A > 1 \quad (15)$$

where A is an arbitrary scaling factor equal to 6.0 throughout. An equally spaced mesh is then choosen in the new g.c. space Ω. For homogenety, relabeling was employed in the case of STO's as well. The integration range is determined by Ω_{min} (lowest value of Ω), $\Delta\Omega$ (increment) and N.

3. RESULTS AND DISCUSSION

The weight functions play a fundamental role in the ID approach. The choice of the discretization parameters Ω_{min}, $\Delta\Omega$ and N (A is quite arbitrary), which determine the discretization interval, is guided by a look on a plot of the w.f. in a preliminary few points experiment. In order to generate universal basis sets, the discretization interval should include the principal part of various w.f.'s. This point is clarified in Section 3.1.

Nevertheless, it should be emphasized that the w.f.'s, despite of being the principal, are not the only factor which determines the numerical results. Also the kernels[8] are important in this context. However, experience tells us that points corresponding to coefficients lower than 10^{-2} in the ℓ.h.s. of the w.f. have no influence in the results, that is, it is easy to choose Ω_{min}. On the other hand, mean values could be very sensitive to high values of α, even for coefficients lower than 10^{-4}. We can advance that for the energy the points should be chosen only with the aid of the w.f.'s.

3.1. Gaussian Generator Functions

In Figs. 1 to 5 we plot the w.f.'s for the GTO case for the 1s, 2s, 3s, 2p and 3 p orbitals. It should be recalled that these functions are originated by solely 1s and 2p g.f.'s. Since the w.f. have similar shapes and tend to concentrate in the same range for the various atoms, to facilitate the view of the graphs only the nobel and some atoms which merit special attention are shown in Figs. 1 to 4. The position of the remaining w.f.'s may be easily located. For instance, in Fig. 1 all first row atoms w.f.'s are comprised between He and Ne and the second row between Ne and Ar. A similar behaviour is true for the rest of the plots.

The smooth and regular behaviour of the w.f.'s indicate its square integrable, L^2_α, character. The lowest values at the left and the decay at the right indicate clearly the integration range relevant for the correct numerical integration of the GHW-HF eqs. The same criterion may serve to choose integration ranges for smaller sets of atoms or even for each individual atom.

It is interesting to consider the 2s w.f. for Li on Fig. 2. It is clear that points to the left would be necessary to span the relevant Ω space for Li. At this stage, we chose not to increase the integration range for the sole benefit of Li (the obtained energy is satisfactory anyway[2]) but it is clear the demand for very difuse orbitals (note that $\Omega < 0$, this $\alpha < 1$ in this region) for this case. Similar considerations are valid for the 3s orbital of Na (Fig. 3), the 2p orbital of B (Fig. 4) and the 3p orbitals of Aℓ and Si (Fig. 5). This situation would be certainly relevant for atom adapted integration ranges.

3.2. Slater Type Generator Functions

The considerations on integration ranges for GTO's in Section 3.1. are also valid for STO's and need not be repeated. What is more interesting to remark is that in the last case the w.f.'s do not have a neat regular character for the s symmetry, while p type w.f.'s seem rather regular. This is suggestive of the possibility that s w.f.'s, and particularily the 1s, are not L^2_α. To asses this behaviour, on Fig. 6 and 7 we plot the 1s and 2p w.f.'s of Aℓ for two different choices of discretization points. While the 2p w.f. is reproduced, the 1s w.f. is not. One may speculate that the 1s g.f. is close enough to the s HF orbitals so that the w.f. is a distribution (certainly more complicated than a delta distribution).

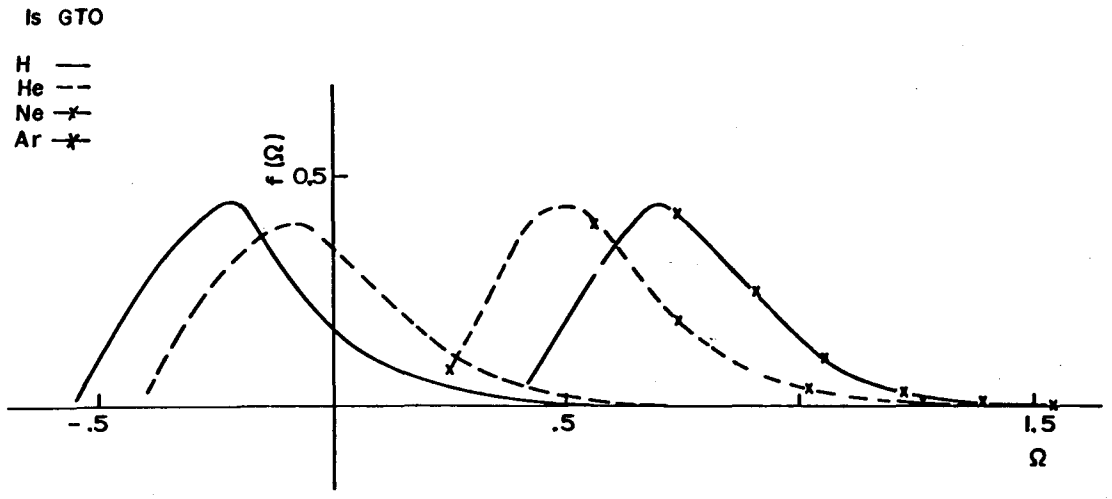

Fig. 1 – The 1s Gaussian w. f.'s for H, He. Ne and Ar.

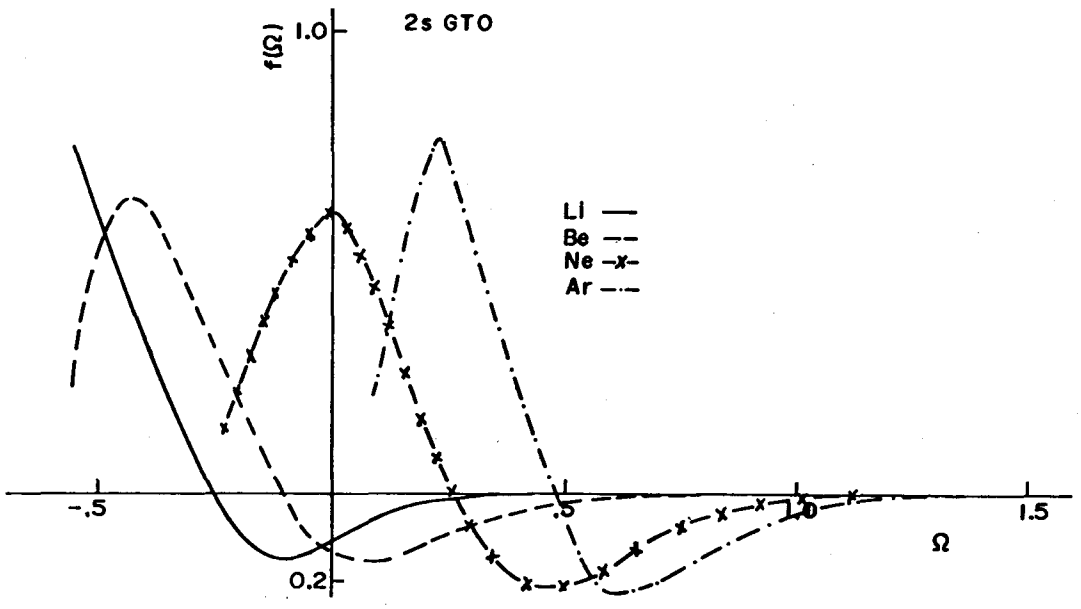

Fig. 2 – The 2s Gaussian w. f',s for Li, Be, Ne and Ar.

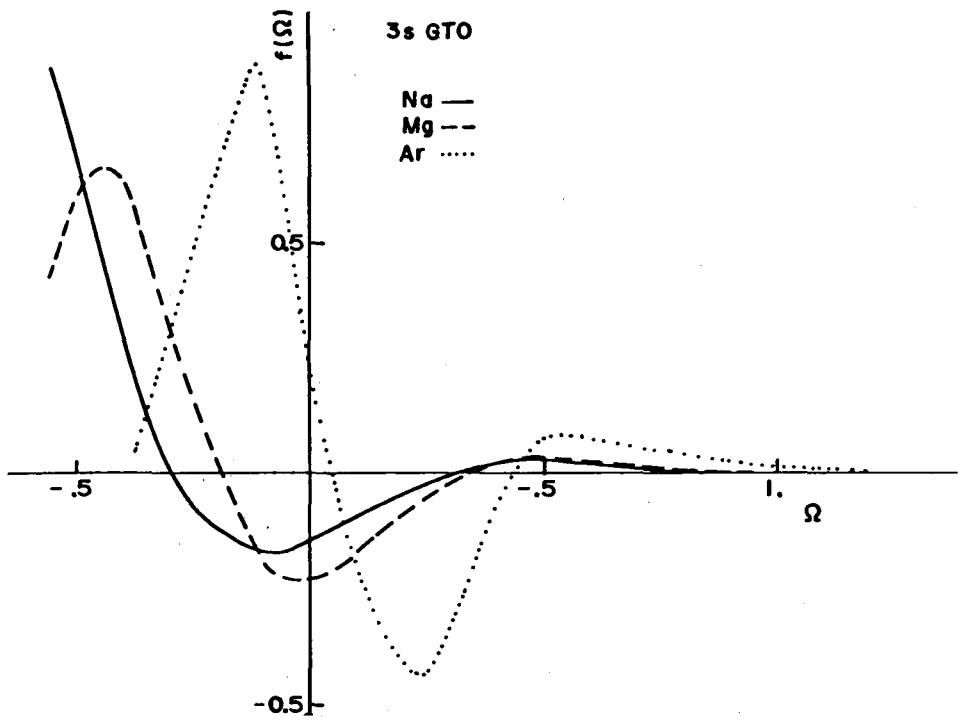

Fig. 3 – The 3s Gaussian w. f's for Na, Mg and Ar.

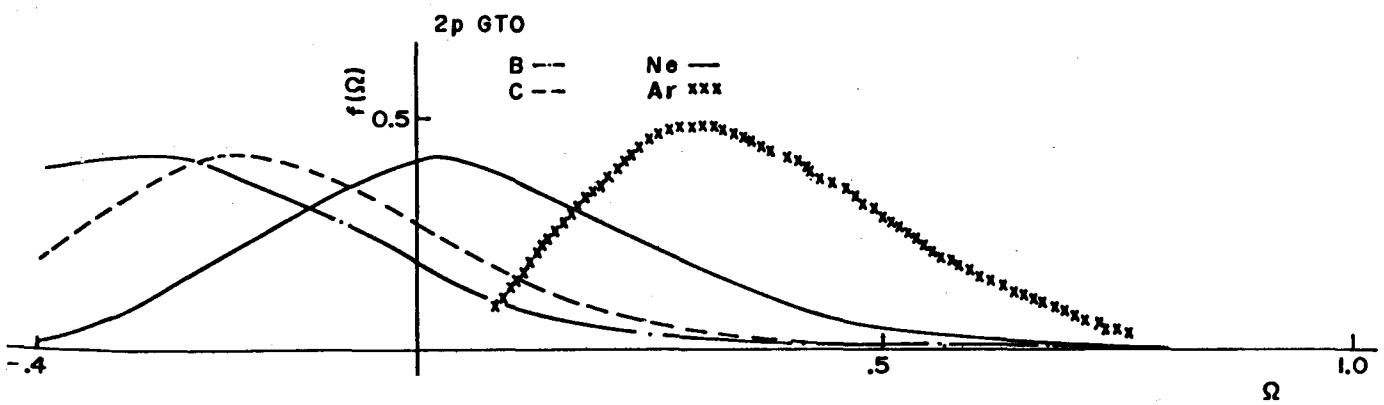

Fig. 4 – The Gaussian w. f.'s for B, C, Ne and Ar.

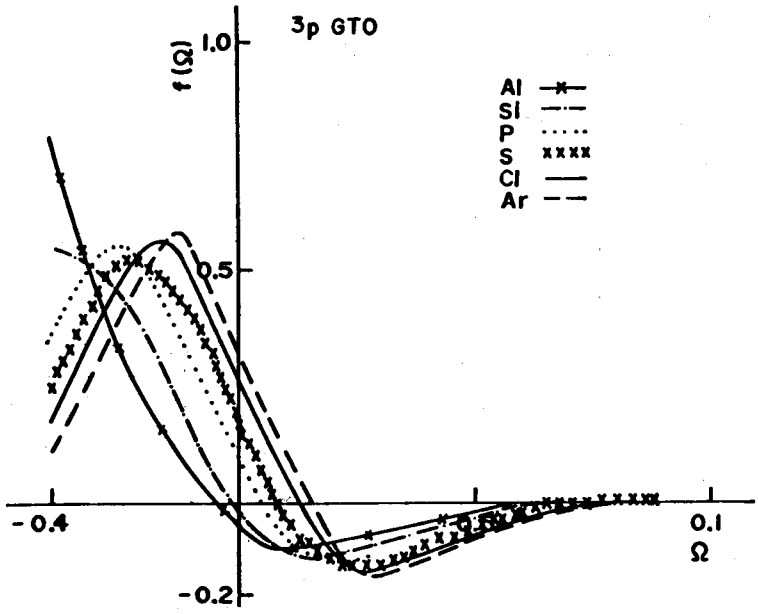

Fig. 5 – The 3p Gaussian w. f.'s for Al to Ar.

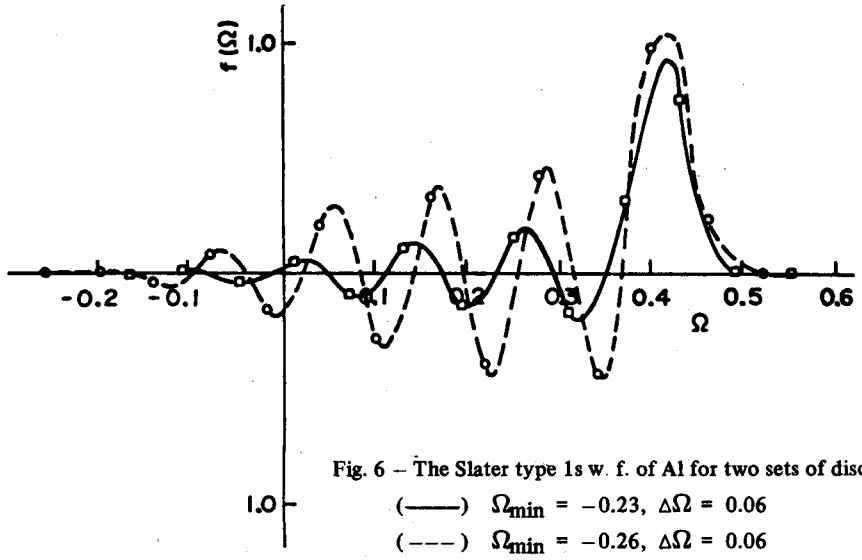

Fig. 6 – The Slater type 1s w. f. of Al for two sets of discretization points (N = 14):
(——) $\Omega_{min} = -0.23$, $\Delta\Omega = 0.06$
(– – –) $\Omega_{min} = -0.26$, $\Delta\Omega = 0.06$

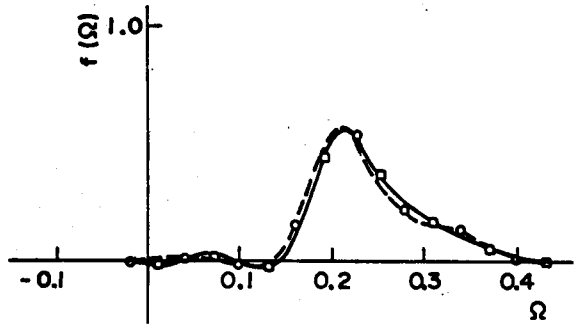

Fig. 7 – The Slater type 2p w. f. for Al for two sets of discretization points (N = 12):
(——) $\Omega_{min} = -0.11$, $\Delta\Omega = 0.06$
(– – –) $\Omega_{min} = -0.14$, $\Delta\Omega = 0.06$

APENDIX

The following universal basis set coefficients are presented:

Apendix I. Universal GTO basis set for Li to Ne;

Apendix II. Universal GTO basis set for He to Ar (coefficients for the H atom are also included);

Apendix III. Universal STO basis set for He to Ne;

Apendix IV. Universal STO basis set for He to Ar (coefficients for the H atom are also included).

In all cases the values for Ω_{min} (lowest value of Ω), $\Delta\Omega$ (increment) and N (number of discretization points) are indicated for each symmetry (s or p). All s basis functions are 1s and all p basis functions are 2p.

To recover the values of the exponents in the original α g. c. space the relation

$$\alpha = \exp(A\Omega); \quad A = 6.0 \tag{A.1}$$

should be used.

The expansion coefficients (discretized w.f.'s) are ordered in columns for each symmetry and each atom. The eigenvalues, ϵ_i (a.u.), are also indicated.

APENDIX I

Discretization parameters

s orbitals	N = 15	$\Omega_{min} = -0.55$	$\Delta\Omega = 0.16$	**A** = 6.0
p orbitals	N = 9	$\Omega_{min} = -0.50$	$\Delta\Omega = 0.16$	**A** = 6.0

Li (^{2}S)		Be (^{1}S)	
1s −2.47595	2s −0.19617	1s −4.73269	2s −0.30928
−0.000105	−0.758515	−0.000320	−0.221361
0.001449	−0.346226	0.001261	−0.625038
0.030283	0.043338	−0.003063	−0.298712
0.302350	0.132167	0.089462	0.071353
0.413865	0.082695	0.386871	0.144083
0.251482	0.044781	0.379347	0.085648
0.108611	0.017445	0.193284	0.038899
0.037724	0.006156	0.075210	0.014088
0.012128	0.001872	0.024754	0.004264
0.003684	0.000596	0.007793	0.001412
0.001143	0.000174	0.002377	0.000440
0.000327	0.000053	0.000700	0.000126
0.000115	0.000017	0.000239	0.000044
0.000020	0.000003	0.000043	0.000008
0.000018	0.000003	0.000037	0.000007

B (^{2}P)		
1s −7.69534	2s −0.49472	2p −0.30987
0.000770	0.030205	−0.147866
−0.002413	0.429063	−0.420007
0.005239	0.557981	−0.382490
0.005941	0.135900	−0.194414
0.239961	−0.144345	−0.065705
0.436397	−0.135035	−0.018918
0.285634	−0.066805	−0.004953
0.122484	−0.026432	−0.000962
0.042793	−0.008819	−0.000282
0.013600	−0.002786	
0.004227	−0.000852	
0.001232	−0.000251	
0.000427	−0.000086	
0.000075	−0.000015	
0.000066	−0.000013	

C (^{1}S)		
1s −11.39158	2s −0.73968	2p −0.31006
0.000267	−0.001391	−0.106613
−0.000846	0.197166	−0.331733
0.002559	0.584632	−0.386296
−0.002612	0.370192	−0.278111
0.108418	−0.060379	−0.122057
0.405342	−0.170957	−0.036494
0.368895	−0.099862	−0.009873
0.176517	−0.042169	−0.001978
0.066047	−0.014677	−0.000597
0.021239	−0.004693	
0.006750	−0.001450	
0.001944	−0.000425	
0.000685	−0.000146	
0.000118	−0.000026	
0.000105	−0.000023	

C (^{3}P)		
1s −11.21552	2s −0.70564	2p −0.43334
0.000262	−0.002465	−0.042042
−0.000862	0.212288	−0.296894
0.002569	0.584392	−0.429813
−0.002378	0.354824	−0.298619
0.108727	−0.059709	−0.125877
0.405143	−0.168332	−0.037695
0.368779	−0.098453	−0.010278
0.178489	−0.041633	−0.002061
0.066034	−0.014484	−0.000623
0.021236	−0.004635	
0.006749	−0.001431	
0.001944	−0.000420	
0.000685	−0.000144	
0.000118	−0.000026	
0.000105	−0.000022	

N (^{4}S)		
1s −15.62904	2s −0.94535	2p −0.56760
−0.000332	−0.002115	0.009229
0.001109	0.083383	0.181888
−0.001761	0.490183	0.406053
0.003987	0.501239	0.369641
0.034384	0.073900	0.193515
0.320742	−0.169257	0.064726
0.423373	−0.131062	0.018031
0.235103	−0.059082	0.003794
0.093396	−0.021672	0.001160
0.030976	−0.006977	
0.009912	−0.002199	
0.002878	−0.000637	
0.001012	−0.000223	
0.000175	−0.000039	
0.000155	−0.000034	

C (^{1}D)		
1s −11.35149	2s −0.71868	2p −0.38134
0.000264	−0.002176	−0.063116
−0.000856	0.206546	−0.315738
0.002568	0.584435	−0.412201
−0.002476	0.360809	−0.289789
0.108601	−0.059925	−0.124449
0.405225	−0.169378	−0.037216
0.368826	−0.099003	−0.010121
0.176501	−0.041845	−0.002027
0.066033	−0.014559	−0.000613
0.021237	−0.004658	
0.006750	−0.001438	
0.001944	−0.000422	
0.000685	−0.000145	
0.000118	−0.000026	
0.000105	−0.000022	

N (^{2}D)		
1s −15.66637	2s −0.96369	2p −0.50867
−0.000333	−0.001825	0.016487
0.001116	0.080338	0.205816
−0.001757	0.485846	0.339463
0.003939	0.507322	0.358319
0.034212	0.075695	0.191397
0.320769	−0.170454	0.064303
0.423454	−0.131779	0.017856
0.235120	−0.059396	0.003752
0.093405	−0.021779	0.001147
0.030978	−0.007013	
0.009913	−0.002209	
0.002878	−0.000640	
0.001012	−0.000224	
0.000175	−0.000039	
0.000155	−0.000034	

N (^{2}P)		
1s −15.69157	2s −0.97636	2p −0.47131
−0.000333	−0.001585	0.023087
0.001121	0.078296	0.220410
−0.001755	0.482808	0.393846
0.003907	0.511517	0.351385
0.034102	0.076872	0.189964
0.320785	−0.171255	0.064016
0.423507	−0.132265	0.017735
0.235131	−0.059607	0.003725
0.093411	−0.021851	0.001138
0.030979	−0.007037	
0.009913	−0.002217	
0.002878	−0.000643	
0.001012	−0.000225	
0.000175	−0.000039	
0.000155	−0.000034	

O (^{1}S)		
1s −20.73019	2s −1.27515	2p −0.55551
−0.000453	0.001353	0.008268
0.001536	0.020414	0.151625
−0.002908	0.348527	0.352350
0.006282	0.575827	0.378672
0.004397	0.225598	0.249360
0.223903	−0.137023	0.097941
0.440875	−0.161473	0.028189
0.294350	−0.079514	0.006135
0.124112	−0.030564	0.001906
0.042876	−0.009997	
0.013737	−0.003190	
0.004056	−0.000922	
0.001410	−0.000325	
0.000249	−0.000056	
0.000217	−0.000050	

O (^{3}P)		
1s −20.66864	2s −1.24436	2p −0.63191
−0.000452	0.001268	0.003364
0.001528	0.021384	0.127206
−0.002911	0.356301	0.352779
0.006302	0.570846	0.391616
0.004583	0.220849	0.253349
0.223964	−0.135843	0.098477
0.440756	−0.160385	0.028420
0.294318	−0.079000	0,006196
0.124099	−0.030385	0.001927
0.042872	−0.009935	
0.013735	−0.003172	
0.004056	−0.000916	
0.001409	−0.000323	
0.000249	−0.000056	
0.000217	−0.000049	

F (^{2}P)		
1s −20.38285	2s −1.57263	2p −0.73001
−0.000251	0.002170	0.000422
0.000859	0.000172	0.081876
−0.001685	0.236215	0.299985
0.004227	0.569635	0.395053
−0.001497	0.351362	0.302298
0.139833	−0.072109	0.136819
0.423688	−0.179785	0.042145
0.348622	−0.100346	0.009402
0.157670	−0.040246	0.003005
0.056741	−0.013499	
0.018291	−0.004331	
0.005745	−0.001261	
0.001889	−0.000443	
0.000338	−0.000077	
0.000292	−0.000068	

O (^{1}D)		
1s −20.69315	2s −1.25651	2p −0.60070
−0.000453	0.001298	0.004997
0,001531	0.020976	0.136903
−0.002909	0.353244	0.353041
0.006294	0.572810	0.386309
0.004508	0.222744	0.251729
0.223939	−0.136311	0.098268
0.440804	−0.160819	0.028328
0.294331	−0.079205	0.006172
0.124104	−0.030457	0.001918
0.042873	−0.009960	
0.013736	−0.003179	
0.004056	−0.000919	
0.001410	−0.000324	
0.000249	−0.000056	
0.000217	−0.000050	

Ne (^{1}S)		
1s −32.77276	2s −1.93060	2p −0.85038
0.000018	0.001520	−0.000213
−0.000047	−0.003803	0.049013
0.000136	0.144992	0.248797
0.000823	0.524804	0.385317
0.001114	0.451484	0.338970
0.077746	0.010908	0.176419
0.381664	−0.185703	0.059238
0.392900	−0.122142	0.013485
0.193596	−0.051116	0.004447
0.072329	−0.017671	
0.023052	−0.005683	
0.007126	−0.001674	
0.002462	−0.000583	
0.000441	−0.000103	
0.000381	−0.000090	

APENDIX II

Discretization parameters

s orbitals	N = 16	Ω_{min} = −0.55	$\Delta\Omega$ = 0.16	A = 6.0
p orbitals	N = 10	Ω_{min} = −0.40	$\Delta\Omega$ = 0.16	A = 6.0

H (^{2}S)		Li (^{2}S)	
1s −0.50000		1s −2.47595	2s −0.19617
0.015843		−0.000104	−0.758515
0.294613		0.001449	−0.346226
0.448226		0.030281	0.043337
0.246394		0.302353	0.132168
0.094863		0.413861	0.082694
0.030907		0.251489	0.044782
0.009759		0.108602	0.017443
0.002935		0.037734	0.006158
0.000904		0.012117	0.001870
0.000268		0.003696	0.000598
0.000082		0.001130	0.000172
0.000024		0.000341	0.000056
0.000007		0.000100	0.000015
0.000002		0.000034	0.000006
0.000000		0.000006	0.000001
0.000000		0.000005	0.000001

He (^{1}S)		Be (^{1}S)	
1s −0.91796		1s −4.73269	2s −0.30928
−0.000670		−0.000320	−0.221359
0.044133		0.001264	−0.065040
0.305251		−0.003070	−0.298712
0.393671		0.089472	0.071354
0.253260		0.386857	0.144080
0.116433		0.379363	0.085652
0.041976		0.193265	0.038895
−0.013651		0.075232	0.014092
0.004188		0.024730	0.004619
0.001285		0.007819	0.001417
0.000384		0.002349	0.000435
0.000118		0.000730	0.000131
0.000034		0.000208	0.000039
0.000012		0.000073	0.000013
0.000002		0.000013	0.000002
0.000002		0.000011	0.000002

B (^{2}P)			O (^{3}P)		
1s −7.69284	2s −0.49317	2p −0.30982	1s −20.66862	2s −1.24433	2p −0.63193
0.000762	−0.029576	−0.391656	−0.000455	0.001264	−0.054520
0.002398	−0.431275	−0.410179	0.001538	0.021367	−0.279301
0.005225	−0.556216	−0.274486	−0.002932	0.356326	−0.404198
0.005974	−0.135923	−0.099759	0.006338	0.570836	−0.316694
0.239941	0.144322	−0.031417	0.004528	0.220854	−0.148334
0.436415	0.134885	−0.008081	0.224040	−0.135858	−0.045793
0.285598	0.066762	−0.001977	0.440655	−0.160360	−0.011727
0.122522	0.026415	−0.000363	0.294439	−0.079027	−0.002594
0.042751	0.008806	−0.000075	0.123963	−0.030354	−0.000477
0.013646	0.002793	−0.000017	0.043023	−0.009970	−0.000132
0.004178	0.000842		0.013573	−0.003135	
0.001285	0.000261		0.004231	−0.000956	
0.000372	0.000074		0.001227	−0.000281	
0.000129	0.000026		0.000427	−0.000096	
0.000023	0.000004		0.000075	0.000017	
0.000020	0.000004		0.000066	−0.000015	
C (^{3}P)			F (^{2}P)		
1s −11.32530	2s −0.70548	2p −0.43328	1s −26.38272	2s −1.57255	2p −0.73004
0.000262	0.002603	−0.194226	−0.000255	0.002164	0.029048
−0.000857	−0.212541	−0.414769	0.000871	0.000190	0.218509
0.002558	−0.584252	−0.366484	−0.001712	0.236202	0.383934
−0.002356	−0.354826	−0.182870	0.004273	0.569660	0.354290
0.108696	0.059712	−0.060763	−0.001567	0.351335	0.195969
0.405183	0.168333	−0.016806	0.139933	−0.072117	0.067057
0.368727	0.098437	−0.004034	0.423554	−0.179757	0.017589
0.176549	0.041645	−0.000843	0.348783	−0.100378	0.004039
0.065968	0.014468	−0.000150	0.157489	−0.040204	0.000740
0.021309	0.004651	−0.000041	0.056944	−0.013545	0.000209
0.006671	0.001414		0.018072	−0.004280	
0.002028	0.000438		0.005711	−0.001315	
0.000598	0.000126		0.001643	−0.000386	
0.000204	0.000044		0.000578	−0.000132	
0.000036	0.000008		0.000100	−0.000024	
0.000031	0.000007		0.000089	−0.000020	
N (^{4}S)			Ne (^{1}S)		
1s −15.62905	2s −0.94534	2p −0.56761	1s −32.77236	2s −1.93040	2p −0.85044
−0.000335	0.002101	0.089456	0.000013	0.001489	0.013699
0.001117	−0.083356	0.346174	−0.000032	−0.003739	0.165270
−0.001777	−0.490217	0.412000	0.000104	0.144948	0.355244
0.004014	−0.501207	0.261507	0.000878	0.524874	0.376472
0.034341	−0.073923	0.101701	0.001029	0.451414	0.240408
0.320799	0.169277	0.029227	0.077871	0.010904	0.092232
0.423299	0.131041	0.007298	0.381495	−0.185671	0.025066
0.235190	0.059103	0.001563	0.393103	−0.122178	0.005942
0.093299	0.021649	0.000285	0.193361	−0.051062	0.001093
0.031883	0.007001	0.000078	0.072594	−0.017731	0.000315
0.009796	0.002173		0.023367	−0.005616	
0.003002	0.000665		0.007435	−0.001746	
0.000882	0.000194		0.002141	−0.000508	
0.000302	0.000067		0.000755	−0.000176	
0.000054	0.000012		0.000130	−0.000031	
0.000047	0.000010		0.000116	−0.000027	

Na (^{2}S)

1s	2s	3s	2p
−40.47520	−2.79397	−0.18175	−1.51506
0.000199	−0.000648	−0.888937	0.000839
−0.000671	0.002134	−0.225770	0.061311
0.001391	0.040042	0.087610	0.301036
−0.001851	0.448931	0.163950	0.414354
0.004527	0.558069	0.099929	0.299644
0.037315	0.106507	0.020540	0.128769
0.325526	−0.182343	−0.029881	0.036563
0.424111	−0.147674	−0.022655	0.008904
0.230768	−0.064611	−0.009978	0.001653
0.089770	−0.023168	−0.003499	0.000483
0.029500	−0.007354	−0.001129	
0.009402	−0.002316	−0.000348	
0.002728	−0.000668	−0.000103	
0.000958	−0.000234	−0.000035	
0.000166	−0.000041	−0.000006	
0.000147	−0.000036	−0.000005	

Mg (^{1}S)

1s	2s	3s	2p
−49.03145	−3.76769	−0.25303	−2.28221
0.000274	−0.002273	−0.434602	0.002259
−0.000923	0.007506	−0.633773	0.013716
0.001925	−0.006059	−0.087424	0.209629
−0.003132	0.321827	0.218449	0.425001
0.006327	0.632459	0.172591	0.354321
0.013397	0.216482	0.048290	0.168920
0.264835	−0.164504	−0.033829	0.050910
0.440393	−0.171576	−0.034113	0.012611
0.268548	−0.079757	−0.015528	0.002397
0.108324	−0.029356	−0.005687	0.000699
0.036471	−0.009414	−0.001815	
0.011623	−0.002980	−0.000575	
0.003408	−0.000860	−0.000165	
0.001188	−0.000302	−0.000058	
0.000208	−0.000052	−0.000010	
0.000183	−0.000046	−0.000009	

Aℓ (^{2}P)

1s	2s	3s	2p	3p
−58.48400	−4.89462	−0.38304	−3.20248	−0.20615
0.000252	−0.001323	−0.137570	0.001767	−0.791310
−0.000855	0.004996	−0.683627	0.000929	−0.239455
0.001788	−0.010425	−0.395479	0.121995	−0.052999
−0.003105	0.190990	0.195908	0.401881	0.103066
0.006135	0.652322	0.282766	0.402886	0.076807
0.002621	0.336417	0.089066	0.211105	0.043230
0.206167	−0.132671	−0.031764	0.068287	0.012733
0.442252	−0.191559	−0.046186	0.017138	0.003430
0.305335	−0.096245	−0.022246	0.003358	0.000596
0.128147	−0.036166	−0.008400	0.000970	0.000194
0.044242	−0.011805	−0.002694		
0.014115	−0.003730	−0.000863		
0.004181	−0.001086	−0.000247		
0.001447	−0.000379	−0.000088		
0.000257	−0.000066	−0.000015		
0.000223	−0.000058	−0.000013		

Si (^{3}P)

1s −68.80522	2s −6.14985	3s −0.53516	2p −4.24947	3p −0.29462
0.000174	0.000491	−0.030654	0.000136	−0.549534
−0.000592	−0.001045	−0.510583	0.001709	−0.446734
0.001241	0.001117	−0.639191	0.058395	−0.140059
−0.002252	0.087691	0.059136	0.350358	0.095858
0.004566	0.616492	0.342239	0.440759	0.101034
−0.001219	0.456849	0.142408	0.254393	0.058285
0.153696	−0.086896	−0.022650	0.088370	0.019283
0.431313	−0.206673	−0.056231	0.022631	0.004987
0.339746	−0.113666	−0.029400	0.004536	0.000960
0.149135	−0.043618	−0.011318	0.001310	0.000287
0.052763	−0.014514	−0.003694		
0.016897	−0.004574	−0.001181		
0.005045	−0.001345	−0.000341		
0.001740	−0.000466	−0.000120		
0.000311	−0.000082	−0.000021		
0.000269	−0.000072	−0.000018		

P (^{4}S)

1s −79.96802	2s −7.50987	3s −0.69547	2p −5.39977	3p −0.39110
0.000078	0.001861	−0.001073	−0.001164	0.348560
−0.000256	−0.005844	−0.328289	0.004054	0.541664
0.000534	0.012111	−0.734373	0.021145	0.262918
−0.001052	0.022399	−0.146492	0.283318	−0.067928
0.002383	0.538186	0.381926	0.463337	−0.123341
−0.001022	0.565095	0.208319	0.298134	−0.075312
0.109488	−0.026836	−0.007544	0.110696	−0.027222
0.409926	−0.216492	−0.063440	0.029247	−0.007033
0.370535	−0.131400	−0.036873	0.005927	−0.001419
0.171154	−0.051760	−0.014381	0.001732	−0.000412
0.061976	−0.017510	−0.004815		
0.019986	−0.005527	−0.001524		
0.005999	−0.001635	−0.000448		
0.002067	−0.000564	−0.000155		
0.000370	−0.000100	−0.000027		
0.000320	−0.000087	−0.000024		

S (^{3}P)

1s −92.00341	2s −9.00399	3s −0.87925	2p −6.68215	3p −0.43714
−0.000021	0.002280	−0.003600	−0.001205	0.243555
0.000067	−0.007458	0.188689	0.005005	0.519157
−0,000144	0.016453	0.717377	0.004185	0.376181
0,000142	−0.009263	0.354955	0.213543	−0.009885
0.000195	0.436630	−0.368894	0.467947	−0.139861
0.000888	0.650207	−0.284344	0.341221	−0.092492
0.074064	0.046967	−0.013734	0.134860	−0.036045
0.380731	−0.220786	0.068153	0.037069	−0.009493
0.396705	−0.148889	0.044728	0.007542	−0.001960
0.194020	−0.060633	0.017716	0.002246	−0.000567
0.071830	−0.020768	0.006082		
0.023397	−0.006599	0.001909		
0.007040	−0.001953	0.000571		
0.002431	−0.000675	0.000195		
0.000435	−0.000120	0.000035		
0.000377	−0.000104	0.000030		

Cℓ (^{2}P)

1s −104.88380	2s −10.60782	3s −1.07292	2p −8.07234	3p −0.50639
−0.000096	0.001870	−0.002298	−0.000724	0.161059
0.000322	−0.006239	0.100629	0.004023	0.474933
−0.000685	0.014431	0.634819	−0.000485	0.457001
0.001114	−0.017237	0.547532	0.150394	0.067981
−0.001615	0.329798	−0.298730	0.454993	−0.147443
0.003102	0.705082	−0.361467	0.382073	−0.110679
0.046988	0.132314	−0.042265	0.160629	−0.045769
0.346315	−0.219059	0.070210	0.046106	−0.012519
0.417549	−0.165673	0.052502	0.009411	−0.002593
0.217497	−0.070199	0.021307	0.002858	−0.000763
0.082280	−0.024276	0.007456		
0.027134	−0.007795	0.002338		
0.008171	−0.002300	0.000705		
0.002834	−0.000800	0.000239		
0.000506	−0.000141	0.000044		
0.000439	−0.000123	0.000037		

Ar (^{1}S)

1s −118.60991	2s −12.32280	3s −1.27736	2p −9.57170	3p −0.59102
−0.000145	0.000985	−0.000578	−0.000283	0.100942
0.000491	−0.003353	0.049049	0.001153	0.417767
−0.001041	0.008521	0.528258	−0.000368	0.506797
0.001768	−0.011782	0.675629	0.098343	0.155020
−0.002870	0.230813	−0.183730	0.427420	−0.141681
0.004876	0.727677	−0.429723	0.419125	−0.128406
0.027264	0.225524	−0.079171	0.187976	−0.055732
0.309016	−0.210670	0.069922	0.056344	−0.016005
0.432673	−0.181466	0.059907	0.011581	−0.003291
0.241299	−0.080369	0.025211	0.003575	−0.000996
0.093291	−0.028045	0.008920		
0.031199	−0.009113	0.002819		
0.009394	−0.002677	0.000850		
0.003277	−0.000939	0.000289		
0.000582	−0.000164	0.000052		
0.000507	−0.000144	0.000045		

APENDIX III

Discretization parameters

s orbitals	N = 9	Ω_{min} = −0.10	$\Delta\Omega$ = 0.07	A = 6.0
p orbitals	N = 6	Ω_{min} = 0.00	$\Delta\Omega$ = 0.07	A = 6.0

He (^{1}S)	
1s −0.91796	
0.010604	
−0.064842	
0.602626	
0.402305	
0.038508	
0.046437	
−0.012756	
0.002682	
−0.000364	

C (^{3}P)		
1s −11.32562	2s −0.70572	2p −0.43337
−0.007674	0.023966	0.348846
0.036762	−0.171492	0.484349
−0.093737	−1.261036	0.172844
0.178240	0.141212	0.064039
−0.288898	0.318548	−0.002018
0.759379	0.292511	0.004385
0.422472	−0.026958	
−0.001530	0.021854	
0.004148	−0.002226	

Li (^{2}S)	
1s −2.47796	2s −0.19632
−0.006988	−1.795486
0.040940	0.618281
−0.125802	0.522063
0.476287	−0.195226
0.605987	0.187736
−0.011011	−0.049912
0.044850	0.025301
−0.009533	−0.006612
0.001022	0.000876

N (^{4}S)		
1s −15.62901	2s −0.94532	2p −0.56759
−0.003520	−0.018261	0.119506
0.016778	0.108250	0.544287
−0.042331	−1.062939	0.256658
0.079559	−0.414981	0.151695
−0.119929	0.241576	−0.002874
0.240031	0.444711	0.007838
0.798494	0.025360	
0.033329	0.016167	
0.006413	0.000102	

Be (^{1}S)	
1s −4.73258	2s −0.30923
0.006811	−0.193848
−0.033230	−1.613454
0.089371	0.875185
−0.193497	−0.041197
0.738917	0.332348
0.396918	−0.008329
−0.007520	0.053284
0.016274	−0.010989
−0.002596	0.001321

O (^{3}P)		
1s −20.66868	2s −1.24431	2p −0.63191
0.004598	−0.023369	0.054001
−0.022094	0.126890	0.465993
0.056732	−0.605968	0.296564
−0.103685	−0.858525	0.244222
0.162201	0.054074	0.018133
−0.219055	0.492970	0.009843
0.948756	0.151154	
0.178086	0.003193	
0.003038	0.003892	

B (^{2}P)		
1s −7.694404	2s −0.49387	2p −0.30991
−0.000246	0.078577	0.825938
0.001080	−0.896241	0.013424
−0.001252	−0.710811	0.263680
0.000816	0.487375	−0.075132
0.029264	0.269513	0.032901
0.894545	0.096726	−0.003748
0.065440	−0.004024	
0.022398	0.010461	
−0.002103	−0.001550	

F (^{2}P)		
1s −26.38277	2s −1.57257	2p −0.73005
0.008845	−0.010969	0.010132
−0.042351	0.056128	0.380797
0.107903	−0.210483	0.322548
−0.196421	−1.035367	0.304246
0.296400	−0.191100	0.064178
−0.393841	0.416672	0.012889
0.811354	0.315975	
0.413312	−0.000791	
0.003209	0.007195	

Ne (^{1}S)		
1s −32.77228	2s −1.93046	2p −0.85047
0.006907	0.003392	−0.010142
−0.032996	−0.017399	0.287485
0.083698	0.050437	0.342745
−0.151199	−1.020099	0.333916
0.224277	−0.406908	0.123314
−0.284649	0.240013	0.021043
0.464844	0.472151	
0.675925	0.018779	
0.021444	0.008975	

APENDIX IV

Discretization parameters

s orbitals	N = 10	Ω_{min} = −0.11	$\Delta\Omega$ = 0.07	A = 6.0
p orbitals	N = 7	Ω_{min} = 0.00	$\Delta\Omega$ = 0.07	A = 6.0

H (^{2}S)
1s −0.50000
−0.041963
0.383345
0.847414
−0.283168
0.140472
−0.067037
0.028210
−0.009741
0.002438
−0.000327

Li (^{2}S)	
1s −2.47795	2s −0.19630
−0.004678	−1.384663
0.028791	−0.250465
−0.088756	1.228859
0.308268	−0.612975
0.732348	0.438167
−0.008151	−0.176823
0.060008	0.086939
−0.014591	−0.030053
0.002933	0.007476
−0.000389	−0.001007

He (^{1}S)
1s −0.91796
0.011733
−0.071147
0.481606
0.528949
0.016748
0.074645
−0.022669
0.006830
−0.001713
0.000229

Be (^{1}S)	
1s −4.73262	2s −0.30925
0.005621	−0.064697
−0.027887	−1.621121
0.076841	0.626167
−0.171440	0.086462
0.569867	0.315551
0.565626	−0.071955
−0.035545	0.055431
0.035633	−0.013264
−0.008222	0.002990
0.000934	−0.000410

B (^{2}P)		
1s −7.69412	2s −0.49392	2p −0.30990
−0.002360	0.070715	−0.832225
0.011484	−0.655779	0.004548
−0.029523	−0.998893	−0.289735
0.059383	0.519647	0.100698
−0.098357	0.232516	−0.050769
0.896883	0.175323	0.012103
0.162542	−0.034235	−0.001995
0.007153	0.025785	
0.003529	−0.005775	
−0.000818	0.000677	

O (^{3}P)		
1s −20.66862	2s −1.24429	2p −0.63189
0.005012	−0.015106	0.056490
−0.024304	0.083350	0.458385
0.063239	−0.374483	0.308363
−0.118575	−1.038899	0.232093
0.190741	0.031871	0.026929
−0.277087	0.405075	0.005611
0.864803	0.263485	0.001034
0.312196	−0.024153	
−0.010212	0.014977	
0.002773	−0.001712	

C (^{3}P)		
1s −11.32561	2s −0.70570	2p −0.43337
−0.004527	0.004470	0.346414
0.022118	−0.029546	0.491500
−0.058120	−1.270915	0.162130
0.116393	−0.022467	0.074773
−0.201468	0.308256	−0.009636
0.530618	0.346422	0.007984
0.619398	−0.022309	−0.000866
−0.032370	0.024671	
0.019944	−0.002520	
−0.002790	0.000135	

F (^{2}P)		
1s −26.38271	2s −1.57253	2p −0.73002
0.004903	−0.000890	0.016217
−0.023784	0.005061	0.362189
0.061842	−0.030351	0.351801
−0.116061	−1.095926	0.273826
0.184724	−0.255819	0.086462
−0.262424	0.299634	0.002062
0.558284	0.421604	0.002667
0.608344	−0.009550	
−0.012523	0.014687	
0.005075	−0.001074	

N (^{4}S)		
1s −15.62905	2s −0.94532	2p −0.56759
0.000687	−0.021975	0.118392
−0.003265	0.129900	0.547681
0.008324	−0.882305	0.251406
−0.013227	−0.649728	0.157086
0.021073	0.243031	−0.006778
0.005964	0.423056	0.009711
0.911729	0.095359	−0.000456
0.067099	−0.003845	
0.011563	0.007570	
−0.001087	−0.001112	

Ne (^{1}S)		
1s −32.77244	2s −1.93040	2p −0.85042
0.001401	0.008824	−0.001999
−0.006786	−0.044850	0.261840
0.017601	0.136192	0.383578
−0.032710	−0.946281	0.290999
0.053256	−0.525437	0.155031
−0.071704	0.141033	0.005503
0.163185	0.521580	0.003861
0.847808	0.050340	
0.032554	0.007398	
0.003589	0.000596	

Na (^{2}S)			
1s −40.47880	2s −2.79727	3s −0.18209	2p −1.51840
−0.002917	0.012357	1.831890	0.002264
0.014167	−0.063681	−0.574088	0.028016
−0.036872	0.180383	−0.725394	0.461400
0.069457	−0.510712	0.337670	0.335614
−0.105667	−1.052087	−0.321407	0.225132
0.147804	0.124280	0.100599	0.022874
−0.173756	0.510946	0.049168	0.004547
0.961355	0.166195	0.035488	
0.135153	−0.005302	0.004265	
−0.000919	0.003135	0.000958	

Mg (^{1}S)

1s −49.03166	2s −3.76766	3s −0.25303	2p −2.28217
−0.005952	−0.001350	0.442226	0.012414
0.028921	0.008267	1.692511	−0.043610
−0.075222	−0.030494	−1.458007	0.304837
0.141378	0.098374	0.166637	0.469535
−0.216643	−1.427639	−0.370440	0.261244
0.295925	−0.074939	0.127047	0.059669
−0.370923	0.537873	0.037705	0.004562
0.926484	0.268206	0.080067	
0.288705	−0.003461	−0.009594	
−0.005255	0.003998	0.001976	

Al (^{2}P)

1s −58.48725	2s −4.89757	3s −0.38488	2p −3.20543	3p −0.20766
−0.006702	−0.013211	−0.069024	0.005628	−1.871027
0.032566	0.065861	1.570514	−0.018168	1.470407
−0.084703	−0.183954	0.071248	0.096971	−0.900631
0.159063	0.410195	−0.880694	0.545473	0.653951
−0.243610	−1.308059	−0.243527	0.326239	−0.179285
0.328761	−0.572659	0.058850	0.095596	0.092694
−0.406082	0.628997	0.067840	0.008019	−0.011100
0.757604	0.342255	0.109988		
0.474902	0.016609	−0.005932		
−0.004725	0.003080	0.001867		

Si (^{3}P)

1s −68.80811	2s −6.15253	3s −0.53706	2p −4.25215	3p −0.29588
−0.005119	0.013552	−0.082799	−0.003500	−1.193378
0.024872	−0.066069	0.732418	0.019033	0.248125
−0.064684	0.176897	1.319152	−0.037702	−0.182111
0.121355	−0.356571	−0.950072	0.499137	0.328397
−0.185591	0.786848	−0.698163	0.433074	−0.006789
0.248575	1.200401	0.139225	0.126872	0.058887
−0.300927	−0.683146	0.056425	0.016109	−0.002093
0.493221	−0.421492	0.145643		
0.669183	−0.045816	0.001192		
0.005893	−0.002137	0.001537		

P (^{4}S)

1s −79.96951	2s −7.51102	3s −0.69639	2p −5.40089	3p −0.39168
−0.001785	−0.004948	0.035372	−0.006739	−0.671834
0.008665	0.023044	−0.215336	0.029966	−0.484584
−0.022511	−0.057324	−1.564819	−0.072013	0.046301
0.042102	0.093696	0.183559	0.353208	0.230642
−0.064260	−0.140695	1.279689	0.553324	0.084353
0.086032	−1.710724	−0.092719	0.161986	0.051673
−0.101235	0.583890	−0.104843	0.028003	0.004222
0.182074	0.539527	−0.157136		
0.845942	0.075189	−0.017626		
0.031501	0.002856	−0.000482		

S (^{3}P)				
1s −92.00474	2s −9.00458	3s −0.87977	2p −6.68280	3p −0.43753
0.002398	0.005831	0.003838	−0.002907	−0.437000
−0.011673	−0.029741	0.012243	0.015203	−0.615026
0.030411	0.083329	−1.286407	−0.035941	−0.147578
−0.057273	−0.187566	−0.716388	0.166205	0.259931
0.087503	0.383274	1.534178	0.648597	0.137171
−0.114913	−1.934362	0.227627	0.210447	0.057105
0.138114	0.278068	−0.233420	0.042804	0.010040
−0.126329	0.702621	−0.147129		
0.981894	0.103080	−0.041654		
0.076169	0.005897	0.000796		

Cℓ (^{2}P)				
1s −104.88484	2s −10.60783	3s −1.07308	2p −8.07258	3p −0.50651
0.006451	0.013310	−0.010728	0.003817	−0.258159
−0.031383	−0.065855	0.087092	−0.011946	−0.662150
0.081716	0.176978	−0.906016	0.028770	−0.298178
−0.153598	−0.363115	−1.282912	−0.007694	0.189932
0.234419	0.656288	1.275381	0.692399	0.225351
−0.308151	−1.824678	0.785376	0.275780	0.057771
0.363638	−0.210485	−0.384542	0.060734	0.018266
−0.387838	0.886709	−0.138546		
1.057960	0.135361	−0.066755		
0.142887	0.010899	0.001269		

Ar (^{1}S)				
1s −118.61056	2s −12.32254	3s −1.27732	2p −9.57175	3p −0.59098
0.009468	0.015127	0.018182	0.010114	−0.131906
−0.046069	−0.074161	−0.108882	−0.040179	−0.648212
0.119974	0.196421	0.604650	0.089246	−0.400254
−0.225483	−0.390213	1.467699	−0.136039	0.052867
0.344074	0.662662	−0.666624	0.677301	0.317944
−0.451913	−1.433515	−1.384378	0.354464	0.062282
0.528940	−0.806681	0.455914	0.083262	0.027395
−0.566630	1.051728	0.163573		
1.060051	0.181147	0.085504		
0.233499	0.017104	0.000132		

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