

Analytical Self-Consistent Field Calculations For Excited Configurations of Cr^{3+}

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Analytical self-consistent field functions were calculated for several states of Cr^{3+} , with two and three open shells of different symmetries. The cusp condition is exactly satisfied. The maximum deviation from the nodal condition for the radial functions $P_{i\lambda}(r)$ is 0.00010.

INTRODUCTION

THE atomic self-consistent field (SCF) calculations based on the expansion method¹ were carried out² for several states of Cr^{3+} , with excited configurations $3d4s4p$, $3d^24s$, and $3d^24p$. The vector coupling coefficients $J_{\lambda\mu\nu}$ and $K_{\lambda\mu\nu}$ were taken from a recent calculation.³ The computation was done with a program⁴ for an IBM-7094 computer.

TABLE I. Calculated energies for states of Cr^{3+} .

Configuration	State	Calculated total energy	Estimate ^a of correlation energy difference
$3d4s4p$	2F	-1039.9956 ^b	...
	4P	-1040.0844	...
	4D	-1040.1132	...
	4F	-1040.1046	...
$3d^24s$	3G	-1040.8733	0.0253
	4P	-1040.9090	...
	4F	-1040.9941	0.0079
$3d^24p$	4G	-1040.7612	-0.0045
	$3d^3$ 4F	-1041.4762 ^c	0

^a Estimates are based on the experimental values given in Ref. 8. The experimental values for any of the three-open-shell configurations, and for the state $3d^24s$, 4P , were not available.

^b The state $3d4s4p$, 2F is an example of a state degeneracy; its calculated total energy is tentative.

^c The value of the ground state $3d^3$, 4F is presented for a comparison (Ref. 6).

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¹ C. C. J. Roothaan and P. S. Bagus, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic Press Inc., New York, 1963), Vol. 2.

² M. Synek and G. E. Stungis, *Bull. Am. Phys. Soc.* **9**, 402 (1964).

³ G. L. Malli and J. P. Olive, Technical Report, Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, 1962-3, Part 2, p. 258 (unpublished).

RESULTS AND DISCUSSION

The notation, the units, and the terminology used are the usual ones and are identical with those employed in the recent works.⁴⁻⁶ Some of the important results are presented in Tables I-V.⁷

It is assumed that the results represent the Hartree-Fock values to at least five significant figures for the total energies and to about three decimal places for the radial functions $P_{i\lambda}(r)$. Registered deviations from the nodal condition for the functions $P_{i\lambda}(r)$ did not exceed 0.00010. The cusp condition was identically satisfied so that the wave functions are particularly accurate in the immediate vicinity of the nucleus.

A comparison with experiment⁸ is presented in Table I. However, no experimental values were available for $3d4s4p$ systems of Cr^{3+} . Otherwise, the comparison was done in a usual way.⁴

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⁴ M. Synek, *Phys. Rev.* **131**, 1572 (1963); **133**, A961 (1964).

⁵ C. C. J. Roothaan and M. Synek, *Phys. Rev.* **133**, A1263 (1964).

⁶ M. Synek and G. E. Stungis, *Bull. Am. Phys. Soc.* **9**, 231 (1964); *J. Chem. Phys.* **41**, 971 (1964).

⁷ The numerical tabulations of the radial wave functions $P_{i\lambda}(r)$ are presented to five decimal places in Tables VI-XIII. These tables are deposited as Document No. 7992 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints, or \$1.25 for 35 mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

⁸ C. E. Moore, *Natl. Bur. Std. U. S. Circ. No. 467*, Vol. 2 (1952).

TABLE II. Optimized exponents ζ of the basis functions for states of Cr³⁺.

Configuration and state Basis function	$3d4s4p$	$3d4s4p$	$3d4s4p$	$3d4s4p$	$3d^24s$	$3d^24s$	$3d^24s$	$3d^24p$
	² F	⁴ P	⁴ D	⁴ F	² G	⁴ P	⁴ F	⁴ G
1s	24.00000	24.00000	24.00000	24.00000	24.00000	24.00000	24.00000	24.00000
3s	26.06679	26.73208	26.62998	25.97661	26.31609	26.31580	26.31599	26.12415
3s	19.17138	18.61096	20.06483	18.89246	18.57013	17.87557	18.95904	18.51175
3s	13.94635	13.51123	13.75373	13.76394	13.38269	13.64407	13.51751	13.51093
3s	10.07813	9.91274	9.92902	9.94962	9.86573	9.93826	9.82248	9.85607
3s	5.29996	5.06227	5.18818	5.25441	5.23393	5.23342	5.24718	5.23161
3s	3.93254	3.76821	3.91230	3.90565	3.77077	3.75939	3.76150	3.72181
4s	2.37851	2.66076	2.29526	2.13364	1.99479	1.98412	1.98706	
4s	1.87540	1.95838	1.88619	1.62264	1.38042	1.14444	1.22444	
2p	12.00000	12.00000	12.00000	12.00000	12.00000	12.00000	12.00000	12.00000
4p	22.10639	22.36884	17.60287	22.37636	22.97001	22.97033	22.97013	22.37281
4p	12.72588	12.72794	11.75429	12.72602	12.84279	12.84056	12.89313	12.69032
4p	9.17024	9.03331	7.74352	9.06363	9.28179	9.26188	9.24274	8.99510
4p	5.78940	5.72133	5.34308	5.69606	5.66891	5.66958	5.65277	5.69233
4p	3.72570	3.70701	3.70221	3.71297	3.62439	3.62370	3.61665	3.67986
4p	2.67148	2.28464	2.20834	2.19689				1.79963
4p	1.69051	1.72923	1.71192	1.73148				1.33847
3d	8.00000	8.00000	8.00000	8.00000	8.00000	8.00000	8.00000	8.00000
5d	10.27369	10.61264	10.34574	10.30436	10.26033	10.66210	10.76425	10.40172
5d	6.92936	7.02285	7.02083	7.00509	7.04276	7.07142	7.05210	7.05092
5d	4.41492	4.43525	4.45619	4.40334	4.38411	4.44640	4.40964	4.45190
5d	2.85983	2.81257	2.98784	2.73282	2.75212	2.90212	2.80212	2.86169
5d					2.34691	2.47339	2.43404	1.66186

TABLE III. Eigenvectors of coefficients $C_{i\lambda p}$ for states of Cr³⁺.

Configuration and state Basis function	$3d4s4p$	$3d4s4p$	$3d4s4p$	$3d4s4p$	$3d^24s$	$3d^24s$	$3d^24s$	$3d^24p$
	² F	⁴ P	⁴ D	⁴ F	² G	⁴ P	⁴ F	⁴ G
1s	0.97984	0.97979	0.97981	0.97984	0.97986	0.97986	0.97987	0.97987
3s	0.02386	0.02122	0.02073	0.02435	0.02290	0.02316	0.02273	0.02373
3s	0.00626	0.01236	0.01012	0.00586	0.00900	0.01014	0.00861	0.00760
3s	0.00222	-0.00320	0.00091	0.00211	-0.00063	-0.00249	0.00019	0.00028
3s	-0.00116	0.00133	-0.00041	-0.00114	0.00009	0.00065	-0.00022	-0.00031
3s	0.00055	-0.00055	0.00020	0.00049	0.00001	-0.00014	0.00010	0.00008
3s	-0.00043	0.00033	-0.00020	-0.00035	-0.00006	0.00002	-0.00010	-0.00007
4s	0.00015	-0.00010	0.00008	0.00010	0.00002	0.00000	0.00002	
4s	-0.00008	0.00004	-0.00005	-0.00006	-0.00001	0.00000	-0.00001	
2s	-0.29377	-0.29379	-0.29372	-0.29381	-0.29374	-0.29384	-0.29375	-0.29731
3s	-0.00062	0.00046	-0.00615	0.00079	0.00002	0.00499	-0.00080	0.00156
3s	0.11175	0.13959	0.10596	0.11984	0.14641	0.15187	0.12865	0.13886
3s	0.44118	0.46075	0.49465	0.45998	0.47069	0.42159	0.48917	0.46698
3s	0.51508	0.46954	0.47440	0.49022	0.45275	0.49375	0.45472	0.46425
3s	0.01883	0.01590	0.01814	0.01289	0.01492	0.01045	0.01166	0.01175
3s	-0.00439	-0.00464	-0.00551	-0.00161	-0.00254	-0.00005	-0.00103	-0.00089
4s	0.00065	0.00079	0.00138	0.00009	0.00037	0.00004	0.00027	
4s	-0.00048	-0.00010	-0.00070	0.00007	-0.00018	0.00008	-0.00001	
3s	0.11211	0.11209	0.11206	0.11209	0.11024	0.11021	0.11011	0.11004
3s	0.00245	0.00060	0.00356	0.00123	0.00070	-0.00096	0.00131	0.00072
3s	-0.05878	-0.06448	-0.04913	-0.05942	-0.06559	-0.07268	-0.05881	-0.06578
3s	-0.14358	-0.16437	-0.18283	-0.15822	-0.16653	-0.13718	-0.17463	-0.15857
3s	-0.38711	-0.35742	-0.35576	-0.37322	-0.34691	-0.36845	-0.34826	-0.35764
3s	0.45367	0.61033	0.49444	0.48611	0.51058	0.51792	0.51375	0.53395
3s	0.72266	0.56976	0.67721	0.69322	0.66841	0.66228	0.66780	0.65200
4s	0.00580	-0.00281	0.01152	0.00745	0.00591	0.00582	0.00608	
4s	-0.00010	0.00386	-0.00315	-0.00147	-0.00139	-0.00058	-0.00065	
4s	-0.04256	-0.04271	-0.04269	-0.04269	-0.03966	-0.04037	-0.04030	
3s	-0.00051	0.00061	-0.00122	-0.00086	-0.00067	-0.00050	-0.00140	
3s	0.02091	0.02058	0.01858	0.02500	0.02626	0.03331	0.02620	
3s	0.05732	0.07232	0.06978	0.05468	0.05298	0.03505	0.05246	
3s	0.15643	0.13803	0.14896	0.16264	0.14596	0.16437	0.15502	
3s	-0.18384	-0.23290	-0.21481	-0.22801	-0.23780	-0.25820	-0.25458	
3s	-0.38569	-0.35790	-0.35197	-0.33677	-0.27872	-0.26803	-0.27204	
4s	0.47454	0.26574	0.53750	0.97585	1.00805	1.05596	1.04618	
4s	0.65919	0.88963	0.58686	0.14147	0.09046	0.04209	0.05188	

TABLE III (continued).

Configuration and state Basic function	$3d4s4p$	$3d4s4p$	$3d4s4p$	$3d4s4p$	$3d^24s$	$3d^24s$	$3d^24s$	$3d^24p$
	2F	4P	4D	4F	2G	4P	4F	4G
	$2p$	$2p$	$2p$	$2p$	$2p$	$2p$	$2p$	$2p$
$2p$	0.72437	0.72438	0.72522	0.72436	0.72429	0.72430	0.72446	0.72440
$4p$	0.00884	0.00826	0.03085	0.00835	0.00750	0.00745	0.00690	0.00851
$4p$	0.22668	0.23058	0.27267	0.23006	0.21914	0.21983	0.21768	0.23302
$4p$	0.12014	0.11936	0.05783	0.11907	0.12813	0.12776	0.13142	0.11615
$4p$	-0.00155	-0.00527	-0.01012	-0.00417	0.00048	0.00010	-0.00145	-0.00373
$4p$	0.00178	0.00330	0.00386	0.00267	0.00062	0.00071	0.00118	0.00213
$4p$	-0.00079	-0.00177	-0.00145	-0.00147				-0.00068
$4p$	0.00008	0.00076	0.00059	0.00080				0.00044
	$3p$	$3p$	$3p$	$3p$	$3p$	$3p$	$3p$	$3p$
$2p$	-0.27359	-0.27364	-0.27361	-0.27365	-0.26763	-0.26758	-0.26746	-0.26762
$4p$	-0.00144	-0.00127	-0.00846	-0.00103	-0.00049	-0.00053	-0.00027	-0.00112
$4p$	-0.08178	-0.08256	-0.08652	-0.08436	-0.08267	-0.08237	-0.08178	-0.08280
$4p$	0.06514	0.07431	0.19725	0.07891	0.07362	0.07348	0.07441	0.08047
$4p$	0.62084	0.63116	0.56904	0.63316	0.62683	0.62640	0.62802	0.60153
$4p$	0.43677	0.40782	0.34618	0.39836	0.40805	0.40841	0.40516	0.42550
$4p$	-0.02775	-0.02088	-0.00162	-0.01548				-0.00070
$4p$	0.00742	0.01043	0.00325	0.01008				0.00262
	$4p$	$4p$	$4p$	$4p$				$4p$
$2p$	0.09597	0.09976	0.10212	0.10288				0.09433
$4p$	-0.00022	-0.00008	0.00225	-0.00002				0.00020
$4p$	0.03279	0.03295	0.03494	0.03373				0.02984
$4p$	-0.04015	-0.04201	-0.09778	-0.04208				-0.03615
$4p$	-0.22527	-0.24830	-0.21744	-0.26649				-0.24556
$4p$	-0.26013	-0.21584	-0.21144	-0.20138				-0.15914
$4p$	0.23246	0.29279	0.43138	0.37281				0.91914
$4p$	0.93496	0.83672	0.70625	0.75032				0.16580
	$3d$	$3d$	$3d$	$3d$	$3d$	$3d$	$3d$	$3d$
$3d$	0.20702	0.20561	0.20617	0.20567	0.19384	0.19226	0.19332	0.19475
$5d$	0.05757	0.04705	0.04878	0.05046	0.04518	0.04034	0.04011	0.04438
$5d$	0.36596	0.36815	0.36161	0.36367	0.33682	0.34035	0.35089	0.34037
$5d$	0.45217	0.45230	0.43979	0.45839	0.45873	0.43929	0.44955	0.44532
$5d$	0.11704	0.13271	0.14467	0.13133	0.19424	0.18251	0.19294	0.18983
$5d$					-0.00721	0.02692	-0.00967	0.00370

TABLE IV. Orbital energies ϵ for states of Cr^{3+} .

Orbital	Configuration and state		$3d4s4p$	$3d4s4p$	$3d4s4p$	$3d4s4p$	$3d^24s$	$3d^24s$	$3d^24s$	$3d^24p$
	2F	4P	4D	4F	2G	4P	4F	4G		
$1s$	-222.69320	-222.68208	-222.67701	-222.67948	-222.28270	-222.27870	-222.26640	-222.30563		
$2s$	-28.65066	-28.64098	-28.63626	-28.63907	-28.19258	-28.18872	-28.17551	-28.21304		
$3s$	-5.45966	-5.45104	-5.44616	-5.44838	-5.10506	-5.10189	-5.09401	-5.12767		
$4s$	-1.37488	-1.46394	-1.46219	-1.46297	-1.28673	-1.29710	-1.29526			
$2p$	-24.56361	-24.55378	-24.54905	-24.55184	-24.11074	-24.10680	-24.09365	-24.13511		
$3p$	-4.14677	-4.13800	-4.13319	-4.13527	-3.81320	-3.81003	-3.80270	-3.84437		
$4p$	-1.08980	-1.16873	-1.19737	-1.18954				-1.06156		
$3d$	-2.43509	-2.42806	-2.45148	-2.44302	-2.02978	-2.05766	-2.14043	-2.18180		

TABLE V. Virial theorem (values of E_p/E_k) for states of Cr^{3+} .

Configuration	State	E_p/E_k
$3d4s4p$	2F	-2.0000108
	4P	-2.0000263
	4D	-2.0000182
	4F	-2.0000074
$3d^24s$	2G	-2.0000197
	4P	-2.0000128
	4F	-2.0000192
$3d^24p$	4G	-2.0000101