CHAPTER V

DATA AND RESULTS

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## 5.1 Energy Spectra

The necessary parameters required for construction of the potential are obtained from spectroscopy. Because the energy spectra are usually given in cm<sup>-1</sup>(hoore, 1949) while the required unit needed in our construction is the rydberg unit, we divide the quoted energy spectra by the hydberg number  $(109,737 \text{ cm}^{-1})$ . Normally, the spectra tables give splitting levels of a degenerate state. Because our calculation do not need the various energy levels of the degenerate state, we average the degenerate state by using the splitting factor for each energy level as a weighting factor.

The energy spectra in the rydberg unit,  $\mathcal{E}_{W}(exp)$ , of the alkali series are given in table 5.1. The energy levels with less than seven digits are given for core states (Slater, 1950).

#### 5.2 Na Effective Potentials

5.2.1 The Prokofjew's potential

The Na potential constructed by Prokofjew(1929) is tabulated in table 5.2

5.2.2 The Newly Constructed Na Potential

The quantization condition is quite good for f states when we assume Q(q) = q. We have calculated  $f_{min}$  for each state and get the following results.

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State	Li	Na	K	Rb	Cs
1s	4.77	79.4	266.2	1120.1	· · ·
2s	.3962944	5.2	28.2	152.7	
3s	.1483677	•3777265	3.0	24.3	
4s	.0772330	.1431617	.3190406	2.7	
5s	.0472749	.0751718	.1724254	.3070228	
6s	.0318910	.0462662	.0688855	.1235474	.2862062
7s	.0229580	.0313262	.0431543	.0672491	.1172939
ິຣ			.0295698	.0423219	.0646062
9s			.0215211	.0290880	.0409713
2p	.2604767	2.8	. 22.2	134.5	
5p	.1144745	.2231020	1.81	18.3	
4p	.06;9510	.1018732	.2003574	1.56	
5p	.0407495	.0583927	.0938248	.1909486	
6p	.0282167	.0378395	.0547219	.0904379	.1809736
7p			.0358757	.0531516	.0867583
8p			.0253471	.0350253	.0514193
3d	.1112146	.1118770	.1227911	8.7	
4d	.0625491	.0628870	.0693704	.1306410	1 L
5d	.0400261	.0402139	.0439642	.0722000	.1535402
6d	.0277931	.0279069	.0302017	.0455874	.0801211
7d	.0204191		.0219741	.0310743	.0407200
4f	.0624870	.0625240	.0627157	.0623702	.0631920
5f	.0399390	.0400243	.0401348	.0402191	.0404178
6f		.0277902	.0278561	.0279150	.0280404
7f		.0204169	.0204608	.0204994	.0205817
Sf		.0156345	.0156627	.0156886	.0157448

Table 5.1 Energy spectra,  $\mathcal{L}_{nl}(exp)$ , of the alkali series

٩	== 0	to .01	Q(g) =	118
	= .01	.15	trong and the	$-26.49^{2} + 11.53900264$
	= .15	1.00		$-2.84 g^{2} + 4.46 g + .5275$
	=1.00	1.55	-	$1.508 p^2 - 4.236 p + 4.876$
	=1.55	3 <b>.3</b> 0		.119682+.20728+1.319
	=3.30	6.74	12	.0005 p + .9933 p + .0222
	=6.74	00	12	P

Table5.2 The Prokofjew Na potential

state	Smin
4f	8.26
5 <b>f</b>	7.14
6 <b>f</b>	6.76

We now let

 $Q_0(q) = p$ ,  $6.76 < q < \infty$ . (5.2.1)

Using the energy spectral data, we get for the d states (eq.(4.3.18))

state	d1	Pmin
3d	.010090	3.89
4d	.000581	3.39
5d	.008385	3.23
6d	.003356	3.16

After averaging the above  $\alpha_1$  s and computing  $\beta_1$  and  $\delta_1$  (eq.(4.3.21)) we have

 $Q_1(\varsigma) = .008853 \varsigma^2 + .880307 \varsigma + .404561, 3.16 < \varsigma < 6.76, (5.2.2)$ The results of our determination of the parameters of  $Q(\varsigma)$  for 1s state are

# state End \$5 \$5 \$5 Smin Smax

1s 79.4 -26.7606 11.50 5 -.005457 .011565 .16

Wor the new interval, we let

$$Q_{g}(q) = 11 p$$
,  $0 < q < .01$  (5.2.3)

Since Sprin of 2p state in matching with the 1s state is found to be .157, we get

 $Q_{5}(q) = -26.7606 p^{2} + 11.6083 q - .003457$ , .01 < q < .16 (5.2.4)

By matching the np states with the (n-1)s states, we get

state	d4	Smin
Sb	-1.53484	1.06
3p	-4.33031	1.70
1+2p	-3.19875	2.50
17D	-2.24,58	4.56
6p	-1.14699	5.03

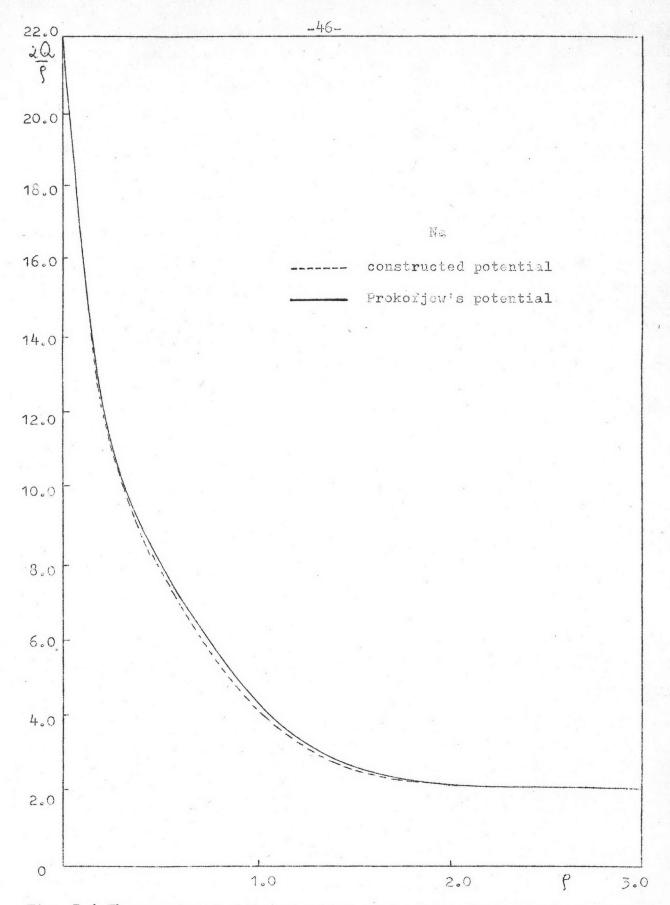
Using the same procedure used on the d states, we get

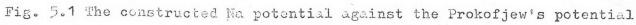
$$Q_4(p) = -2.51082p^2 + 3.99244p + .594502, .16$$

The two matching functions are (see oppendix D)

$$Q_{3}(p) = 1.79219 p^{2} - 5.12992 p + 5.42936, 1.06 < g < 1.70 (5.2.6)$$
$$Q_{2}(p) = -.009933 p^{2} + .995241 p + .222965, 1.70 < g < 3.16 (5.2.7)$$

The total result is tabulated in table [...] and is plotted in Wig.5.1 against the Probofjew potential.





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P	#	0	to	.01	Q(g) =	119
	=	.01		.16	25	-26.76069 <sup>2</sup> +11.6083p003457
	22	.16		1.06		-2.5108282+3.992448+.594502
		1.06		1.70		$1.79219g^2 - 5.12992g + 5.42936$
	==	1.70		3.16	=	$009333 p^{2} + .995241 p + .222965$
	=	3.16		6.76	=	·00885392+.8803079+.404.561
	=	6.76		00	=	P
	=	6.76		00	=	P

Table 5.3 The constructed Na potential

5.2.3 The Na Potential with Polarization

When the polarization term is inserted, we have to determine the parameter S. The S for 4f state is chosen because it is the lowest state among other f states. This determination gives

 $Q_{g}(q) = q + .525262/q^{2}, \quad 8.24 < q < \infty$  (5.2.8)

The other steps are the same as those mentioned in section 5.2.2. The result is tabulated in table 5.4.

9	=	0	to	.01	/		119
		.01		.16	2	2	-26.760692+11.60839003457
		.16		1.06	i ya sa B	-	$-2.51082 p^{2} + 3.99244 p + .594502$
	17	1.05		1.70	=	=	$1.726759^2 - 4.991219 + 5.35584$
	=	1.70		3.20	=	=	.037617p2+.751858p+.474231
	-	3.20		8.24			0008019 +.9977328 +.080832
	=	8.24		8	-	:	g + .525262/g2

Table 5.4 The constructed Na potential with polarization

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# 5.3 Li Effective Potentials

## 5.3.1 The Seitz's Potential

The corrected Seitz's potential as published by Kohn and Rostoker (1954) which has been converted to Q(q) by multiplying -rV with  $\rho/2$  is tabulated in table 5.2. It should be noted that Q(q) for  $\rho$  greater than 3.72 is equal to q.

9	Q(g)	٩	Q(P)	P	Q(p)	P	Q(P)	P	Q(g)
.02	.0573	.20	. 4762	•56	.87385	1.24	1.3662	2.44	2.4678
.O4	<b>.1</b> 109	.24	.5476	.50	.90414	1.32	1.4296	2.60	2.6161
.06	.1635	.20	.6104	.68	.96563	1.40	1.4945	2.76	2.7690
.03	.2140	•32	:66534	.76	1.0215	1.42	1.5607	2.92	2.9245
.10	.2627	•36	.71055	.84	1.0778	1.64	1.6972	3.08	3.0823
.12	.3094	•40	•74720	.92	1.1151	1.80	1.0419	3.24	3.2413
.14	•3541	.44	•77944	1.00	1.1883	1.96	1.9919	3.40	3.4007
.16	.3968	.48	.01113	1.08	1.2451	2.12	2.1505	3.56	3.5604
.18	.4375	.52	<b>.</b> 84284	1.15	1.3026	2.20	2.3133	3.72	3.7202

Table 5.5 The Seitz's Li potential

5.3.2 The Newly Constructed Li Potential

By using procedure similar to those applied to Ha in section 5.2.2 ,we obtain

$$Q_{0}(9) = 9$$
,  $7.14 < 9 < \infty$  (5.3.1)

 $Q_1(g) = .000915 g^2 + .986934 g + .046646 , 3.26 < g < 7.14 (5.3.2)$ 

It is found that  $\beta_{\min}$  for 2p state by matching with  $Q(\rho)$  is 6.31. Thus  $\beta_{\min}$  of  $Q_1(\rho)$  is equal to 6.31. This point is then used in the determination of parameters for  $Q_2(\rho)$ . The result is

$$Q_2(q) = .004041 q^2 + .947620 q + .170195, 1.21 < q < 6.31 (5.3.3)$$

#### We shall not go into numerical details for

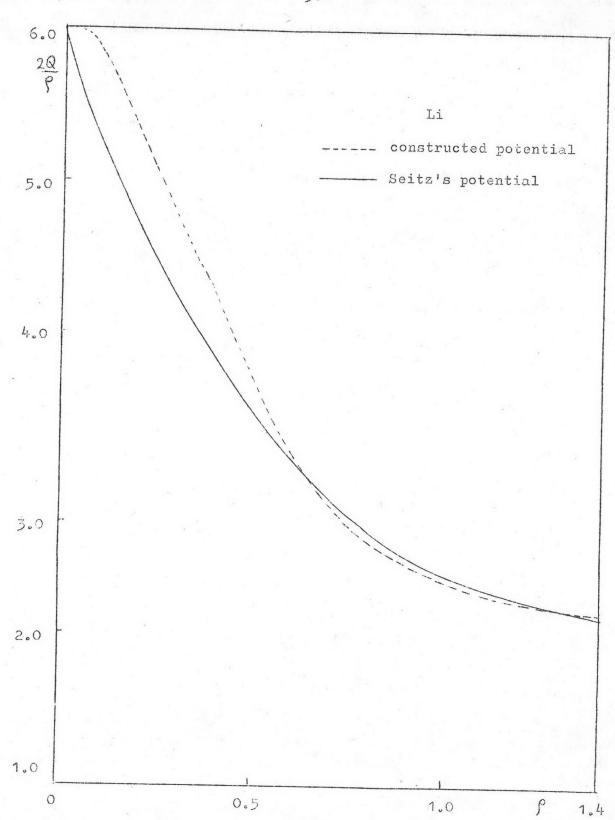
the next calculations but will tabulate the total result in table 5.6 . The result is plotted in Fig. 5.2 against the Seitz's potential.

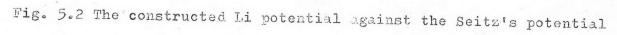
P	=	O	to .04	Q(g) =	39
	-	.04	.58	=	$-2.75058p^{2} + 3.23736p005121$
	=	. 58	<b>。</b> 90	=	1.02024p2-1.13679p+1.26338
	=	.90	1.21	122	. 415525 g 048308 g +. 773565
		1.1	5.31		.004041 8 + . 9474848 + . 171111
	• •	6.31	7.14	=	·000915 p2+ ·986934 p+.046646
	=	7.14	8	=.	P

Table 5.6 The constructed Li potential

5.3.3 The Li Potential with Polarization

The contribution from polarization is chosen to occur in in the nearest f state, 4f , and the total result is tabulated in table 5.7 .





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23	0	to .04	((g))	=	39
=	.04	•5G			-2.75058 p <sup>2</sup> + 3.23736 p005121
==	•	.90		a. 	.972673p2-1.081629+1.24738
	.90	1.24			.447067 p - 135523 p + .821639
11	1.24	7.47		aansa Jaree	.001816p2+.968699p+.137022
=	7.47	0.25		=	.000593p2 +.986966p +.068796
=	3.25	00			p+.110593/p2
		= 0 = .04 = .50 = .90 = 1.24 = 7.47 = 3.25	= .04 .50 = .50 .90 = .90 1.24 = 1.24 7.47 = 7.47 0.25	= .04 .50 = .50 .90 = .90 1.24 = 1.24 7.47 = 7.47 0.25	= .04 .50 = $= .50 .90 =$ $= .90 1.24 =$ $= 1.24 7.47 =$ $= 7.47 0.25 =$

Table 5.7 The constructed Li potential with polarization

# 5.4 Potential Testings

5.4.1 By Using the QDN (Semiclassical Nethod)

We test the constructed potentials by calculating energy levels and then compare them with the experimental data. The calculation is performed by employing the QDM. We may recall the relation between the quantum defect and the potential in chapter III. The relation can be re written as

$$\mu(E) = \bar{I}_1 - \bar{I}_2 \qquad (5.4.1)$$

where  $I_1$  and  $I_2$  stand for the terms in the right hand side of eq. (3.3.28) respectively.

 $^{\rm I}_2$ , the coulomb term, can be analytically integrated and is a constant for a given energy level. The energy level can then be determined after we obtain the quantum defect. The results are shown in tables 5.0 and 5.9. It should be noted that the Simpson's integration formula is employed to compute some integral for which the analytical integration formula is not available (Appendix B).

state	Endexp)	I <sub>2</sub>	Ene(Prok)	Ene(No.1)	Eng(No.2)
3s	.3777265	1.127089	.385864	.377282	.374133
45	.1431617	2.142935	.144658	.142236	.141740
5s	.0751719	5.147306	.075661	.074762	.074573
6s	.0462662	4.149101	.046492	.046057	.045964
Зр	.2231020	0.617174	.211206	.204029	.202649
4p	<b>.</b> 1010 <b>7</b> 33	1.630068	.098492	.096154	.095737
5p	.0583927	2.630288	.056965	.055932	.055755
6p	<b>.037</b> 3396	5.640753	.037103	.036563	.036470
3d	.1118770	0.490169	.111145	.111744	.112049
4d	.0620870	1.488331	.062521	.062900	.062889
5d	.0402159	2.486685	.040012	.040227	.040200
6d	.0279070	3.486093	·027785	.027915	.027892
4f	.0625241	0.499229	.062500		
5f	.0400243			.062500	.062508
51 6f		1.498482	.040000	.040000	.040024
	.0277902	2.498659	.027778	.027778	.027795
7f	.0204170	3.498485	.020408	.020408	.020418

Table 5.8 Energy levels reproduced from constructed Na potentials  $\mathcal{E}_{ul}$  (Prok),  $\mathcal{E}_{ul}$  (No.1),  $\mathcal{E}_{ul}$  (No.2), and  $\mathcal{E}_{ul}$  (exp) are the energy levels reproduced from the prokofjew's Na potential, the constucted Na potentials in tables 5.3 and 5.4, and the experimental energy levels respectively.

state	Enl(exp)	I <sub>2</sub>	Ene(Seitz)	Eu(10.3)	En(No.4)
25	• 2962944	1.088514	.3344	.418188	.418887
3s	.1485678	2.096152	.1459	.152871	.152949
45	.0772330	5.098310	.0763	.073888	.078902
5 <b>s</b>	.0472749	4.099225	.0468	.048054	.048063
65	.0318910	5.09971	.0316	.032321	.032328
SЪ	<b>.260476</b> 8	0.459366	.2583	.261604	.261930
Зp	.1144745	1.455600	.1143	<b>.1144</b> 88	.114421
4-p	.0639511	2.454358	.0639	.063926	.063890
5p	.0407495	3.453804	.0407	.040729	.040710
бр	.0282167	4.453151	.0282	<b>.02</b> 8198	.028189
3d	.1112146	0.498604	.1111	.111344	.111616
4d	.0625491	1.498430	.0625	.062645	.062741
5d	.0400262	2.498363	.0400	.040082	.040127
6d	.0277932	3.498335	.0278	.027828	.027855
7d	.0204192	4.498108	.0204	.020440	.020456
4f	.0624871	0.500413	.0625	.062500	.062465
5 <b>f</b>	.0399390	1.503617	.0400	.040000	.039893

Table 5.9 Energy levels reproduced from constructed Li potentials  $\epsilon_{wl}$  (Seitz),  $\epsilon_{wl}$ (No.5),  $\epsilon_{wl}$ (No.4), and  $\epsilon_{wl}$ (exp) are the energy levels reproduced from the Seitz's Li potential, the constructed Li potentials in tables 5.6 and 5.7, and the experimental energy levels respectively.

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5.4.2 By Using Quantum Mechanical Method

The ground state energy level of Na atom is calculated numerically using the procedure given by Dumrongsak (1976) in order to compare with that reproduced from the Frokofjew's potential. This calculation may be called "integration" because we are able to find the value of wave function at the fourth point after the first three values have been known or determined.

In our calculation, the asymptotic radial wave function ( for  $f \rightarrow O$ ) is needed because we start the calculation at the point f = 0 which the radial wave function vanishes. The second and the third points can be obtained from the asymptotic wave function  $f \in \mathcal{P}$  which we adapt from the asymptotic s-state radial wave function of Hydrogen-liked atom given by Fark (1964) instead of f which was used by Dumrongsak. We have performed the outward integration only. If the radial wave function vanishes as f tends to infinity, the energy required for the integration to be possible will be the required energy. We can use larger intervals for larger radial distance because the radial wave function does not fluctuate at the outer region. However, we must roset appropriate first-three points of integration for the new intervals. For example, if we have a table of integration with an interval of .08

ρ U 4.08 .178855 4.16 .172059 4.24 .172502 4.32 .168237 4.40 .156775

and we want to double the interval of integration to be .16 i.e. calculate

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the wave function U at  $\rho = 4.56$ , 4.72,....; we must reset first-three points to be

$$\begin{array}{cccc}
\rho & U \\
4.08 & .174996 \\
4.24 & .170602 \\
4.40 & .156775 \\
4.56 & \dots \\
4.72 & \dots \end{array}$$

We can use new finite differences of the first-three points to determine U at  $\rho = 4.56, 4.72, \ldots$ . Dumrongsak made an error because he used the table

			9		U	
		{	4.24	c	170602	
first-three	points	3	4.32		168237	
		C	4.40		,156775	
			4.56			
			4.72	- 6		

The calculated value of U at  $\rho = 4.56$  had an error because of the the misuse of the first-three points which led to an error of the derivative at the point  $\rho = 4.40$ .

We have calculated several wave functions for some assumed ground state energies by using the Prokofjew's potential. The wave function which vanishes at infinity will give the ground state energy predicted by this potential. It is found that the ground state energy is inbetween .3800 and .3815 rydberg which is the same as those shown in the first paper of Wigner and Seitz (1933). The wave functions for those two assumed energies are given in table 5.10 and 5.11 and plotted in Fig.5.3. It should be noted that we have neglected the decimal decimal point and following zeros in the table. One of them cuts the axis and the other blows up. This implies that the ground state energy should be inbetween those two assumed energies.

When our constructed Na potential is used instead of the Prokofjew's potential, the predicted ground state energy is found to be in the interval .37889 and .37895 rydberg. Our result deviates from the experimental value by about 0.3 % while that reproduced from the Prokofjew's potential gives an error about 0.9 %. The calculated wave functions obtained by using our potential are given in tables 5.12 and 5.13 and also plotted in Fig.5.3.

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P	U	P	U	P	U	ρ	U
.0025 .0050 .0075 .0100	002432 4732 6906 8953	.32	- 40021 - 44307 - 48075 - 51326		102 <b>4</b> 96 107094 111522 11 <b>5</b> 781		112115 106585 101157 95850
.015	10876 12680 14368	. 1.	- 54071 - 56321	1.34	119872 123799		90678 85653
.020	15944 17412		- 58096 - 59413 - 60295	1.92	127561 131162 134604		8078 <b>5</b> 76080 71542
.025	18775		- 60765 - 60846	2.08	141022		67173 62974
.030	21203 23254 24955		- 60563 - 59934 - 58995		146836 152071 156752		58946 55084 51388
	26331 27407		_ 57759 _ 56252		160903 164549		47852 44473 41244
	28205 28746 29050	-	- 54495 - 52 <b>51</b> 1		167716 170429	8.56	38160 35215
.08	29135 29020	.72	- 50318 - 47938 - 45389		172710 174585 176076	8.88	32401 29713 27142
.09	28721 28254 27633	.76	- 42687 - 39850 - 36894		177205 177993	9.20	24682
.10	26873 25985	.80	- 33832		178461 178628 178514	9.52	20062 15790 11804
. 11	23876 21394	.84	- 27448 - 20797 - 13964		1 <b>7</b> 8136 177512 176658		8040 4431
	18614 15604		- 7020 - 27		175590 174324		911 - 2592
	12418 9108 5714		6967 13923		172875 171257 169484		
	2273 1187		20809 27601 34279	4.08	167570 165526		-
-	4638 8059 11432		40829 47239 53500	4.24	163365 161098 158737		
6.0	14741 17972		59606 6 <b>55</b> 52	4.40	156290		
.26	21115 24160 27098		71334 76951 82399	4.56	151182 145847 140346		
.28 _ .30 _	29925 32634		87679 92788		134738 129070		30
- 00 -	35222		97727		123387		

Table 5.10 The wave function for  $\mathcal{E}_{30} = .3800$  rydberg by using the

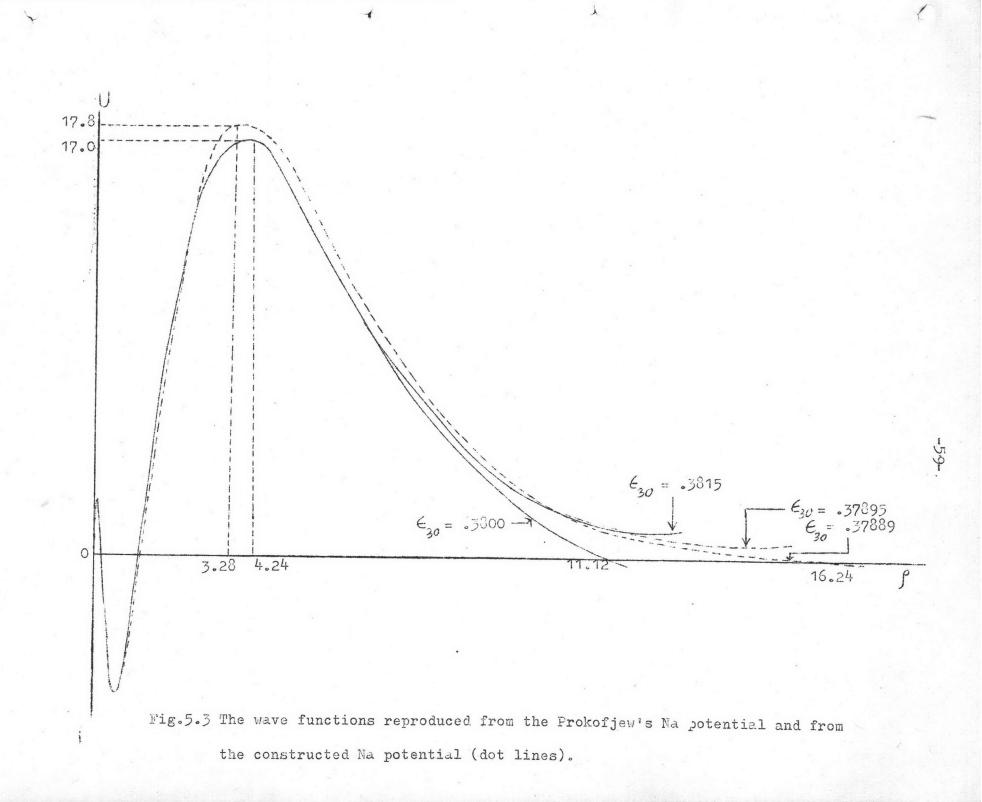
Prokofjew's Na potential

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βU	P U	ΡU	P	Ü
.0025	- 32643 .30 - 35231	76965 82415	4.56	152142 146902
The same as	.32 - 40051	87697 92308		141501 135997
those given in	- 44517 - 48084	97750 102521		130439 124869
table 5.10	- 51336 - 54080 - 56330	107121 111552		119326
	- 58104 - 59422	115814 1.84 119909		108441 103149
	- 60304 - 60775	123839 1.92 127606		97984 92961
	- 60854 - 60570	131211 2.00 134657	-	88093 83389
	- 59944 - 59002	2.08 141085		78856
	- 57765	146911 :152158		70322
	- 56257 - 54500	156852 161018		62511 58877 55420
	- 52515 - 50323	164680 167864		52139
	- 47943 .72 - 45393 - 42691	170595 172896		49031 46090
	- 42091 .76 - 39854 - 36897	174791 176304	8.56	43313
.11 23875	.80 - 33835	177456 178269 178762 178956	8.88	38232 35917
<b>21</b> 392 18612	.84 - 27450	178956 178870	9.20	33745 31712
15600 12414	- 20798 - 13964	178522 177928	9.52	28041 24862
9103 5709	- 7020 - 26	177105 176070		22137 19831
- 1195	6969 13926	174838 173424		17912 16354
- 4645 - 8056	20813 27606	171842 170107	$(x_i) \in \mathcal{N}_{i}$	15134 14235
- 11440 - 14749	34285 40836	168250 4.08 166226		13644
- 17981 - 21123	47247 53509	164105 4.24 161880		13355 13369
.26 - 24168	59616 65563	159561 4.40 157159	3	
- 28 - 29934	71347		l	

Table 5.11 The wave function for  $\epsilon_{30} = .3815$  rydberg by (using the Prokofjew's potential

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p U	P U	, p U	, P U
.0025 .00243 .0050 473 .0075 690 .0100 895 1088 1269 1438 .020 1597 1744 .025 1880	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	98531 10,413 108144 112723 1.84 117149 121423 1.92 125544 129512 2.00 133328	120487 114777 109173 103695 98360 93182 88171 85335
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{ccccccc} 2.08 & 140507 \\ 147091 \\ 153091 \\ 158524 \\ 163406 \\ 167755 \\ 171591 \\ 174936 \\ 177810 \\ 180235 \\ 182233 \\ 185823 \\ 185833 \\ 185833 \\ 186390 \\ 186578 \\ 186466 \\ 186074 \\ 185421 \\ 184526 \\ 186466 \\ 186074 \\ 185421 \\ 184526 \\ 183406 \\ 182078 \\ 130559 \\ 178363 \\ 177007 \\ 4.08 & 175004 \\ 172868 \\ 4.24 & 170611 \\ 168246 \\ 4.40 & 165784 \\ 4.56 & 160614 \\ 155181 \\ 149555 \\ 143801 \\ 137972 \\ 132117 \\ \end{array}$	$\begin{array}{r} 78680\\ 74209\\ 69925\\ 65826\\ 61913\\ 58184\\ 54634\\ 51262\\ 48062\\ 45029\\ 8.56\\ 42159\\ 39445\\ 8.88\\ 36883\\ 34465\\ 9.20\\ 32187\\ 9.52\\ 28023\\ 24343\\ 21102\\ 18254\\ 15758\\ 15758\\ 15758\\ 15574\\ 11668\\ 10006\\ 8557\\ 7297\\ 6198\\ 5241\\ 4405\\ 3672\\ 3027\\ 2456\\ 1944\\ 1481\\ 1056\\ 657\\ 15.92\\ 274\\ 16.24 - 101\\ \end{array}$

Table 5.12 The wave function for  $\xi_{30} = .37889$ by using the constructed Na potential

<u>p</u> U p U .0025	P	98531	م ا	138013
		103413		132162
		108144		126326 120541
7	1.84	112723 117150		120541
		121424		109236
	1.92	125545		103763
	2.00	129513 13 <b>3329</b>		98443 93261
The same as those given				88256
in table 5.12	2.08	140508 147092		83426 78778
		153093		74314
		158525		70036
		163 <b>407</b> 167757		65945
		171593		62040 58319
		174938		54779
		177813		51416
		180238 182 <b>2</b> 37		48226 45204
		183830	8.56	42345
		185040		39643
		185889 186397	8.88	37094
		136585	9.20	34690 32427
		136474		-
		186083 185431	9.52	28296
		184537		24654 21456
		183418		18659
		182091		16221
		180573 178879		14105 12277
		177024		10707
	4.08	175022		9365
		172887		8228
	4.24	170632		7275 6487
	1. 1.0	168268	102 J	5850
	4.40	165808		5350
	4.56	160641		4977 4725
		155211		4725
		149589 143838		4568
	1	0000	15.28	4661

Table 5.13 The wave function for =.37895

by using the constructed Na potential