Calculations of Rydberg energy levels for Ni XVIII using the weakest bound electron potential model theory

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Martin expression about the quantum defect of single-valence atoms is extended to many-valence atoms by identifying the weakest bound electron (WBE) under the weakest bound electron potential model (WBEPM) theory. Six Rydberg series energy levels of $2p^6np^2P^\circ_{1/2}$ ($n \geq 3$), $2p^6np^2P^\circ_{3/2}$ ($n \geq 3$), $2p^6nd^2D_{3/2}$ ($n \geq 3$), $2p^6nd^2D_{5/2}$ ($n \geq 3$), $2p^6nf^2F^\circ_{5/2}$ ($n \geq 4$), and $2p^6nf^2F^\circ_{7/2}$ ($n \geq 4$) for Ni XVIII are calculated by this method. The calculated results are in good agreement with the experimental results.

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Recently, atom and ion spectra research, especially energy level and radiative lifetime in high Rydberg states, is playing a more and more important role with the high-tech development in astrophysics, laser physics, physical chemistry, and nuclear fusion. Corresponding measurement and computation techniques are developing quickly[1−3]. In respect of theoretical methods, the presentation and development of quantum defect theory (QDT) provides a feasible way to calculate the high Rydberg state. For example, the multichannel quantum defect theory (MQDT) has made great achievements in Rydberg spectrum analysis for atoms and ions[4,5]. However, there are too many parameters to be fitted in MQDT, and its computing process is rather complex. The weakest bound electron potential model (WBEPM) theory[6−9] developed in recent years is a simple and effective method for calculating Rydberg state energy levels. In WBEPM theory, if one can categorize the electrons in atoms or ions into the weakest bound electron (WBE) and non-weakest bound electron (NWBE), appropriate Rydberg state energy level series could be extracted. Moreover, single-valance electron system problems can be translated into many-valance electron ones. Then, Martin expression[10] can be extended to calculate Rydberg state energy levels for complicated atoms or ions with many-valance electrons. In this paper, based on WBEPM theory, the Rydberg series energy levels $2p^6np^2P^\circ_{1/2}$ ($n \geq 3$), $2p^6np^2P^\circ_{3/2}$ ($n \geq 3$), $2p^6nd^2D_{3/2}$ ($n \geq 3$), $2p^6nd^2D_{5/2}$ ($n \geq 3$), $2p^6nf^2F^\circ_{5/2}$ ($n \geq 4$), and $2p^6nf^2F^\circ_{7/2}$ ($n \geq 4$) of Ni XVIII are calculated, and the results agree well with experimental values.

For alkali atoms and alkali-like ions, their energy levels and spectral terms can generally be written as (in Rydberg unit)

$$E_n = -\frac{1}{(n-\delta)^2} = -\frac{1}{n^{*2}}, \tag{1}$$

$$T = \frac{R}{(n-\delta)^2} = \frac{R}{n^{*2}}, \tag{2}$$

where δ is the quantum defect, representing the penetrating interaction between the valance electron and the atomic core; δ is approximately a function of angular-momentum quantum number l for alkali atoms; n is the principal quantum number, and $n^* = n-\delta$ is the effective principal quantum number. For the given series l, n^* is a function of n, and R is the Rydberg constant.

In WBEPM theory, all the extranuclear electrons of atoms (or ions) can be categorized into either WBE or NWBE. WBE is such an electron that has the weakest connect with the system among all electrons. So it is also the most active electron that is excited or ionized most easily in the system. When WBE is excited, it will form various electronic configurations. For a given configuration series, their energy level is only a function of the principal quantum number n[7], and the relationship between the energy level values of atomic system and the effective parameters of WBE can be expressed as

$$T = \frac{RZ'^2}{n'^2}, \tag{3}$$

where Z' is the effective nuclear-charge number of WBE, representing a stronger interaction between WBE and the atomic core (such as orbital penetration); n' is the effective principal quantum number of WBE, representing a weaker interaction between them (such as atomic core polarization). In QDT, atomic (or ionic) energy level is often denoted by spectral term, which is

$$T = T_{\text{limit}} - \frac{RZ'^2}{n'^2}, \tag{4}$$

where T_{limit} is the ionization limit of the corresponding spectral series.

In terms of WBE, if we attribute all the interactions between WBE and atomic core to the change of effective principal quantum number, the concept of quantum defect will be applied to WBEPM theory through transformation

$$\frac{Z'}{n'} = \frac{Z_{\text{net}}}{n^*} = \frac{Z_{\text{net}}}{(n-\delta)}, \tag{5}$$

where Z_{net} refers to the net nuclear-charge number of atomic core (for atom: $Z_{\text{net}} = 1$), and $n^* = \frac{n'}{Z'}Z_{\text{net}}$,

$\delta = n - n^*$ refers to the quantum defect number. Then Eq. (4) becomes

$$T = T_{\text{limit}} - \frac{RZ_{\text{net}}^2}{(n - \delta)^2}. \tag{6}$$

In QDT, Martin[10] expanded δ to an infinite series and reserved the former four terms, namely Martin expression becomes

$$\delta = a + bm^{-2} + cm^{-4} + dm^{-6}, \tag{7}$$

and $\qquad m = n - \delta_0, \quad \delta = n - n^*, \tag{8}$

where δ_0 is the quantum defect number of the lowest energy level in a given Rydberg state series; a, b, c, and d are the fitted spectral coefficients. Due to the restriction of experimental condition, there is generally lack of the lowest energy level in measurement of Rydberg state energy levels for atoms (or ions). However, if we replace the lowest energy level in Eq. (8) by the lowest one in the experimental energy levels, we can calculate the regularities of Rydberg series energy levels for atoms (or ions) through Eqs. (6) − (8).

The six Rydberg spectral series energy levels of Ni XVIII $2p^6np^2P^{\circ}_{1/2}$ $(n \geq 3)$, $2p^6np^2P^{\circ}_{3/2}$ $(n \geq 3)$, $2p^6nd^2D_{3/2}$ $(n \geq 3)$, $2p^6nd^2D_{5/2}$ $(n \geq 3)$, $2p^6nf^2F^{\circ}_{5/2}$ $(n \geq 4)$, and $2p^6nf^2F^{\circ}_{7/2}$ $(n \geq 4)$ are calculated with Eqs. (6) − (8). The coefficients a, b, c, d in Eq. (7) fitted with experimental data from Ref. [1] are listed in Table 1. The calculated values using WBEPM and the experimental values of each energy series, namely T_{cal} and T_{exp}, are all listed in Tables 2 − 4, respectively. In order to compare with other theoretical calculations, the energy values T_{DHF} calculated by Ray[1] using fully relativistic Dirac-Hatree-Fock (DHF) method are also listed in Tables 2 − 4. The values for calculating T_{cal} are 109736.29 cm^{-1} for R and 4896200 cm^{-1} for T_{limit}[11].

Tables 2 − 4 show that our results are very close to the experimental data with a relative deviation generally no

Table 1. Spectral Coefficients of the Six Energy Level Series for Ni XVIII by Fitting the Experimental Values in Martin Expression

Configuration	a	b	c	d	δ_0
$2p^6np^2P^{\circ}_{1/2}$ $(n \geq 3)$	0.204286	−0.356076	7.94682	−35.2052	0.215102
$2p^6np^2P^{\circ}_{3/2}$ $(n \geq 3)$	0.181306	0.310052	−1.64013	5.54423	0.205761
$2p^6nd^2D_{3/2}$ $(n \geq 3)$	0.0717042	−0.0950856	1.70001	−11.1222	0.0661464
$2p^6nd^2D_{5/2}$ $(n \geq 3)$	0.0650764	0.0939157	−0.594257	−2.22785	0.0644936
$2p^6nf^2F^{\circ}_{5/2}$ $(n \geq 4)$	0.00839609	−0.0692479	4.17243	−54.2438	0.00708246
$2p^6nf^2F^{\circ}_{7/2}$ $(n \geq 4)$	0.0209116	−1.1979	33.9513	−296.05	0.00631232

Table 2. Theoretical and Experimental Energy Values of $2p^6np^2P^{\circ}_{1/2,3/2}$ (cm^{-1})

n	$2p^6np^2P^{\circ}_{1/2}$			$2p^6np^2P^{\circ}_{3/2}$		
	T_{exp}	T_{cal}	T_{DHF}	T_{exp}	T_{cal}	T_{DHF}
3	311860	311861	313143	342460	342460	344286
4	2426120	2426120	2424615	2438130	2438130	2436914
5	3352440	3352440	3324793	3358070	3358070	3354612
6	3839360	3839360	3361489	3843200	3843200	3839044
7		4127299	3974221		4130149	4152017
8		4311742	4173434		4313899	4309601
9		4436978			4438632	
10		4525888			4527173	
11		4591276			4592287	
12		4640761			4641567	
13		4679111			4679763	
14		4709432			4709965	
15		4733818			4734259	
16		4753723			4754091	
17		4770180			4770491	
18		4783943			4784207	
19		4795568			4795795	
20		4805477			4805673	

Table 3. Theoretical and Experimental Energy Values of $2p^6nd^2D_{3/2,5/2}$ (cm^{-1})

n	$2p^6nd^2D_{3/2}$			$2p^6nd^2D_{5/2}$		
	T_{exp}	T_{cal}	T_{DHF}	T_{exp}	T_{cal}	T_{DHF}
3	765550	765550	768810	770200	770200	773807
4	2594350	2594576	2593328	2596490	2596442	2595583
5	3433540	3433406	3430231	3434600	3434663	3431407
6	3885590	3885078	3881446	3886050	3886069	3882130
7	4155060	4155787	4125839	4156630	4156558	4125449
8	4330990	4330727	4326902	4331290	4331321	4327192
9		4450271			4450730	
10		4535558			4535917	
11		4598529			4598812	
12		4646341			4646567	
13		4683495			4683678	
14		4712938			4713089	
15		4736666			4736791	
16		4756068			4756172	
17		4772134			4772222	
18		4785588			4785662	
19		4796966			4797030	
20		4806675			4806730	

Table 4. Theoretical and Experimental Energy Values of $2p^6nf\,^2F^\circ_{5/2,7/2}$ (cm^{-1})

n	$2p^6nf\,^2F^\circ_{5/2}$			$2p^6nf\,^2F^\circ_{7/2}$		
	$T_{\exp}$	T_{cal}	T_{DHF}	$T_{\exp}$	T_{cal}	T_{DHF}
4	2666150	2666150	2664120	2667010	2667010	2664921
5	3468980	3468981	3465837	3469300	3469238	3466250
6	3905760	3905759	3901817	3905980	3906104	3902057
7	4168880	4168881	4164748	4169020	4168918	4164900
8	4339530	4339530	4335386	4339330	4339360	4335487
9		4456466			4456206	
10		4540080			4539798	
11		4601929			4601657	
12		4648960			4648711	
13		4685555			4685333	
14		4714588			4714393	
15		4738008			4737837	
16		4757173			4757024	
17		4773055			4772925	
18		4786363			47862497	
19		4797625			47975256	
20		4807240			48071523	

more than $1.75 \times 10^{-2}\%$. Further, our accuracy is better than Ray's[1]. The largest deviation is in $2p^67d\,^2D_{3/2}$ level, and the main reason is that there may be some perturbation states near the level. The much higher energy levels, in comparison with experimental values unavailable, are predicted in the tables mentioned above. Considering the high accuracy of the foregoing calculated values, our forecasted values are reliable. The results prove that the extended Martin expression is suitable for the

spectral series of the many-valence electron Ni XVIII.

In conclusion, this paper provides an effective way for calculating the Rydberg state energy levels for Ni XVIII, whose computing process is both compact and accurate and needs fitting few parameters. Meanwhile, it also provides a new idea in studying the Rydberg spectra for other many-valence electron atoms.

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