

Analytical wave functions for atomic quantum-defect theory

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We present an exactly solvable effective potential that reproduces atomic spectra in the limit of exact quantum-defect theory, i.e., the limit in which, for a fixed l , the principal quantum number is modified by a constant: $n^* = n - \delta(l)$. Transition probabilities for alkali atoms are calculated using the analytical wave functions obtained and agree well with accepted values. This allows us to make phenomenological predictions for certain unknown transition probabilities. Our analytical wave functions might serve as useful trial wave functions for detailed calculations.

Rydberg noted¹ that the spectra of many atoms have series given approximately by

$$E_{n^*} = -E_0/n^{*2}. \tag{1}$$

In modern notation, E_0 is a constant with dimensions of energy and n^* is

$$n^* = n - \delta(l), \tag{2}$$

where n is a positive integer, the principle quantum number, and $\delta(l)$ is approximately constant for a given fixed orbital quantum number l , $l \geq 0$. Spectra given by Eqs. (1) and (2) are called Rydberg series, and their study is known as quantum-defect theory.

The quantum defect $\delta(l)$ phenomenologically models the effective charge, generated by the $Z - 1$ core electrons and the nucleus of charge Z , by shifting the energy eigenvalues away from the hydrogenic values. For example, the low-lying s orbitals of lithium may be described² by the values $n^* = 1.588, 2.596, 3.598$, etc., rather than by the hydrogenic values $n = 2, 3, 4$, etc. In the modern approach to quantum-defect theory,³ the quantum defect $\delta(l)$ is defined as the phase shift of an exact atomic wave function relative to Coulomb wave functions beyond a core radius.

As Cowan has summarized,³ the standard approach to quantum-defect theory usually proceeds either with de-

tailed many-body calculations or with calculations using a multiparameter effective potential that is fitted to atomic energy levels. We call "exact quantum-defect theory" the limit in which $\delta(l)$ for fixed l is exactly constant for all n , as distinct from the more general case for which $\delta(l)$ varies by a few percent with n . In this paper, we observe that, in the limit of exact quantum-defect theory, there is an analytically solvable effective potential that yields the "exact" quantum-defect eigenvalues.

To establish our notation, we summarize the hydrogen-atom solution. The radial equation may be written as

$$[-d^2/dy^2 - 1/y + l(l+1)/y^2 - E_n] \chi_{nl}(y) = 0, \tag{3}$$

where $E_n = -1/4n^2$, $y = \beta r$, and $n \geq l + 1$. Here, $\beta = 2\mu e^2/\hbar^2$ represents two inverse Bohr radii; also, we use y rather than the standard variable $\rho = y/n$. The normalized radial wave function $R_{nl} = \chi_{nl}/r$ is given by

$$R_{nl}(y) = n^{-2} [\beta^3 \Gamma(n-l)/2\Gamma(n+l+1)]^{1/2} \times (y/n)^l \exp(-y/2n) L_{n-l-1}^{(2l+1)}(y/n), \tag{4}$$

and satisfies the usual orthonormality condition

$$\int_0^\infty dr r^2 R_{nl} R_{n'l} = \delta_{nn'}. \tag{5}$$

Note that we use associated Laguerre polynomials $L_{n-l-1}^{(2l+1)}(y/n)$ defined by

$$L_n^{(\alpha)}(x) = \sum_{p=0}^n (-x)^p \Gamma(n+\alpha+1)/[p!\Gamma(p+\alpha+1)\Gamma(n-p+1)], \tag{6}$$

instead of the related $L_{n+l}^{2l+1}(y/n)$ often used in quantum mechanics,⁴ which are defined by

$$L_n^j(x) = d^j L_n(x)/dx^j, \tag{7}$$

where L_n are the ordinary Laguerre polynomials. Equation (7) is valid for integer j only. This distinction will be important in the following discussion.

Returning to exact quantum-defect theory, we propose the following equation⁵ to model the effective radial equation of the valence electron in the presence of the quantum defect:

$$[-d^2/dy^2 - 1/y + l(l+1)/y^2 + V_{\text{eff}}(y) + 1/4n^{*2}] y R_{n^*,l^*}(y) = 0. \tag{8}$$

Here, $V_{\text{eff}}(y)$ is chosen to satisfy

$$l(l+1)/y^2 + V_{\text{eff}}(y) = l^*(l^*+1)/y^2, \tag{9}$$

$$l^* = l - \delta(l) + I(l), \tag{10}$$

for integer $I(l)$. The range of possible integers $I(l)$ will be discussed later. A glance at the hydrogen equation shows that the potential $V_{\text{eff}}(y)$ yields a solution with the same functional form as Eq. (4) but with noninteger values of n^* and l^* .⁶ It is here that the definition (6) plays a critical role.

Thus, the eigenvectors are

$$R_{n^*l^*}(y) = n^{*-2} [\beta^3 \Gamma(n-l-I)/2\Gamma(n^*+l^*+1)]^{1/2} (y/n^*)^{l^*} e^{-y/2n^*} L_{n-l-I-1}^{(2l^*+1)}(y/n^*), \quad (11)$$

with eigenenergies given by Eq. (1). The solution still involves the associated Laguerre polynomials because n^*-l^*-1 is equal to $n-l-I-1$, an integer. The eigenvectors (11) are therefore normalizable, and in our convention they obey the orthonormality condition

$$\int_0^\infty dr r^2 R_{n^*l^*} R_{n'^*l'^*} = \delta_{n^*n'^*}. \quad (12)$$

The usual spectroscopic notation designates energy levels as though they are hydrogenic, so that the wave functions are expected to have $n-l-1$ nodes. This means that the number of nodes in our wave functions can be unusual, since it is given by the order of the associated Laguerre polynomial, $n-l-I-1$. Thus, for example, if $I=0$ or 1 the physical ground state of the $l=0$ lithium Rydberg series, designated as the $2s$ level, would have one or zero nodes, respectively, even though $n^*=1.588$. The node counting is important for an interpretation of the phenomenologically determined integer I , as is discussed below.

The solution (11) may be used to calculate expectation values. Due to the factor n^* in the expression $\rho=y/n^*$, it is easiest to perform the integration using the expression (6) for the associated Laguerre polynomials in terms of products of Γ functions. For a transition from the level (n_i, l_i) to the level (n_f, l_f) , the expectation value of $y^d = (\beta r)^d$ is

$$\begin{aligned} \langle n_f^*, l_f^* | y^d | n_i^*, l_i^* \rangle &= \frac{1}{2} (n_i^* n_f^*)^{-2} (n_i^*)^{-l_i^*} (n_f^*)^{-l_f^*} F_n^{l_i^*+l_f^*+d+3} [\Gamma(n_i^*-l_i^*)\Gamma(n_f^*-l_f^*)\Gamma(n_i^*+l_i^*+1)\Gamma(n_f^*+l_f^*+1)]^{1/2} \\ &\times \sum_{p=0}^{n_i^*-l_i^*-1} \sum_{q=0}^{n_f^*-l_f^*-1} (-F_n/n_i^*)^p (-F_n/n_f^*)^q \\ &\times \Gamma(l_i^*+l_f^*+d+p+q+3) / [\Gamma(p+1)\Gamma(q+1)\Gamma(n_i^*-l_i^*-p)\Gamma(n_f^*-l_f^*-q) \\ &\times \Gamma(2l_i^*+p+2)\Gamma(2l_f^*+q+2)], \quad (13) \end{aligned}$$

where $F_n = 2n_i^* n_f^* / (n_i^* + n_f^*)$. As required, Eq. (13) satisfies the orthonormality condition (12).

Observe that Eq. (13) has $(n_i^*-l_i^*) \times (n_f^*-l_f^*)$ closed-form terms, each of which is a product of Γ functions. Therefore, all of our subsequent calculations can in principle be done by hand, on the back of an (admittedly large) envelope.

We may test the eigenvectors (11) by computing transition probabilities for selected atoms. The transition probability T_{fi} for the transition of a valence electron from the level (n_i, l_i) to the level (n_f, l_f) is⁴

$$T_{fi} = (\pi\alpha^3 \nu_R / 6) [(n_f^*)^{-2} - (n_i^*)^{-2}]^3 \times F_l |\langle n_f^*, l_f^* | y | n_i^*, l_i^* \rangle|^2, \quad (14)$$

where the fine-structure constant α is given by $\alpha = e^2/\hbar c$, the Rydberg frequency ν_R is given by $\nu_R = \mu e^4 / 4\pi\hbar^3$, and where F_l is an l -dependent factor given by

$$F_l = \begin{cases} l_i / (2l_i + 1), & l_f = l_i - 1 \\ (l_i + 1) / (2l_i + 1), & l_f = l_i + 1. \end{cases} \quad (15)$$

We have used Eq. (14) to compute probabilities of transition between a variety of levels of the elements lithium and sodium. The $s \rightarrow p$ and $p \rightarrow s$ transition probabilities should provide the most stringent test of the model, because they involve the largest quantum defects. For higher values of l , the asymptotic quantum defects are

zero, so the eigenstates become hydrogenic.

The value of the integer $I(l)$ was varied with l and was thus selected separately for the initial and final states. The allowed range of variation of $I(l)$ is determined by two conditions. First, requiring the kinetic and potential energies to be separately normalizable imposes the constraint $l^* + \frac{1}{2} > 0$, i.e., $\delta(l) - l - \frac{1}{2} < I(l)$. Second, the Laguerre polynomials $L_{n-l-I-1}^{(2l^*+1)}(y/n^*)$ defined by Eq. (6) exist only for $I(l) \leq n_{\text{min}} - l - 1$, where n_{min} is the principal quantum number of the physical ground state. Thus, for example, for the lithium s orbitals $-0.1 < I(l) \leq 1$; therefore, $I(l)$ can only take the values of 0 and 1.

Table I lists the results for lithium, along with accepted transition probabilities.⁷ The asymptotic quantum defects² used in our calculations were $\delta(0)=0.40$, $\delta(1)=0.05$, and $\delta(2)=0$. The listed probabilities T_{fi} were obtained with $I(l)=0$ for all l ; this gave the best agreement with accepted values.

In considering Table I, we defer until later a discussion of the special cases of the $2p \rightarrow 2s$, $3p \rightarrow 2s$ transitions and the transition probabilities of order 10^3 Hz. Then, our results always agree with the accepted values to within 10% and in certain cases to within a fraction of a percent. Now, the accepted values, except for $2p \rightarrow 2s$, are considered valid to within about 10%.⁷ Therefore, our results are surprisingly good.

In particular, due to the agreement of the $p \rightarrow d$ transi-

TABLE I. A comparison of our transition probabilities with currently accepted values (Ref. 5) for the lithium atom. The asymptotic quantum defects are $\delta(0)=0.40$, $\delta(1)=0.50$, and $\delta(2)=0$.

Transition	Phenomenological approximation (10^8 Hz)	Accepted value (10^8 Hz)
$3s \rightarrow 2p$	0.337	0.349
$4s \rightarrow 2p$	0.106	0.101
$4s \rightarrow 3p$	0.0744	0.0746
$5s \rightarrow 2p$	0.0486	0.0460
$5s \rightarrow 3p$	0.0285	0.0276
$5s \rightarrow 4p$	0.0224	0.0225
$2p \rightarrow 2s$	0.327	0.372
$3p \rightarrow 2s$	0.0170	0.0117
$3p \rightarrow 3s$	0.0356	0.0377
$4p \rightarrow 2s$	0.0169	0.0142
$4p \rightarrow 3s$	9.07×10^{-5}	3.69×10^{-5}
$4p \rightarrow 4s$	0.00752	0.00772
$4p \rightarrow 3d$	0.00533	0.00552
$5p \rightarrow 3d$	0.00224	0.00231
$5p \rightarrow 4d$	0.00279	0.00286
$6p \rightarrow 3d$	0.00116	
$6p \rightarrow 4d$	0.00136	0.00139
$6p \rightarrow 5d$	0.00139	0.00142
$3d \rightarrow 2p$	0.732	0.716
$3d \rightarrow 3p$	6.04×10^{-5}	3.81×10^{-5}
$4d \rightarrow 2p$	0.248	0.230
$4d \rightarrow 3p$	0.0702	0.0685
$4d \rightarrow 4p$	1.89×10^{-5}	1.28×10^{-5}
$5d \rightarrow 2p$	0.116	0.106
$5d \rightarrow 3p$	0.0361	
$5d \rightarrow 4p$	0.0138	0.0136
$5d \rightarrow 5p$	6.83×10^{-6}	4.78×10^{-6}

tions (within 4%) and the $d \rightarrow p$ transitions (within 10%, except for probabilities of order 10^3 Hz), we consider our phenomenological values of 1.16×10^5 Hz for $6p \rightarrow 3d$ and 3.61×10^6 Hz for $5d \rightarrow 3p$ as predictions to be tested against detailed atomic calculations. Other predictions are also made by our model, but the ones quoted involve lower-lying levels and so provide the best test of its predictive power.

Table II contains a similar listing for sodium. In this case, we used asymptotic quantum defects² $\delta(0)=1.35$, $\delta(1)=0.859$, and $\delta(2)=0.01$. The best match to accepted values was obtained with $I(l)$ values of $I(0)=2$, $I(1)=1$, and $I(2)=0$.

Here, the agreement with accepted values might even be viewed as better than that of Table I. This is because (except for the $3p \rightarrow 3s$ transition) the accepted values are all considered⁷ valid to only about 25% and (except for the $3p \rightarrow 3s$ case) all of our values are within this limit. Therefore, our results for the $5s \rightarrow 4p$, $6s \rightarrow 5p$, $5p \rightarrow 5s$, and $5d \rightarrow 5p$ transition probabilities can again be considered as phenomenological predictions.

Returning now to the special cases, note that our calculations have not allowed for the experimentally observed variation of $\delta(l)$ with n , which is largest for small values of n . Therefore, low-lying levels should be modeled less accurately than those with larger values of n . However,

phenomenological quantum defects $\delta_n(l)$ that vary slightly with n for a given l may be used just as easily to describe the wave functions, although the number of input parameters becomes large and the exact orthonormality relation is gone. We have therefore calculated transition probabilities using wave functions involving the phenomenological quantum defects $\delta_n(l)$.² We find that significant improvement in the agreement occurs for the transition probabilities that are small, i.e., of order 10^3 Hz, in Table I. The cancellations in the overlap integrals are evidently unusually sensitive to the wave functions involved. Similarly, there are also improvements in the $2p \rightarrow 2s$ and $3p \rightarrow 2s$ values of Table I and the $3p \rightarrow 3s$ value of Table II. The relatively large deviation of the "exact" quantum defects of the lowest levels from the phenomenological quantum defects can be important.

The node structure implied by the values of $I(l)$ for sodium is especially interesting, indicating as it does a distinct departure from the standard hydrogenic picture. Since the number of nodes is $n-l-I-1$, the s orbitals have wave functions with two fewer nodes than expected, while the p orbitals have wave functions with one fewer node.

This situation is reminiscent of supersymmetry.⁸ Our results cannot be used as evidence either for or against supersymmetry, however, because the effective potential

TABLE II. A comparison of our transition probabilities with currently accepted values (Ref. 5) for the sodium atom. The asymptotic quantum defects are $\delta(0)=1.35$, $\delta(1)=0.859$, and $\delta(2)=0.01$.

Transition	Phenomenological approximation (10^8 Hz)	Accepted value (10^8 Hz)
$4s \rightarrow 3p$	0.247	0.251
$5s \rightarrow 3p$	0.059	0.072
$5s \rightarrow 4p$	0.0552	
$6s \rightarrow 3p$	0.0253	0.0330
$6s \rightarrow 4p$	0.0159	0.0173
$6s \rightarrow 5p$	0.0167	
$3p \rightarrow 3s$	0.453	0.629
$4p \rightarrow 3s$	0.0261	0.0292
$4p \rightarrow 4s$	0.057	0.062
$5p \rightarrow 3s$	0.0060	0.0060
$5p \rightarrow 4s$	0.0073	0.0074
$5p \rightarrow 5s$	0.0129	
$4p \rightarrow 3d$	0.001 89	0.001 57
$3d \rightarrow 3p$	0.421	0.495
$4d \rightarrow 3p$	0.106	0.131
$4d \rightarrow 4p$	0.062	0.067
$5d \rightarrow 3p$	0.045	0.050
$5d \rightarrow 4p$	0.0240	0.0260
$5d \rightarrow 5p$	0.0154	

V_{eff} in (8) masks the original potential. One cannot tell whether the potential should be $l(l+1)/y^2 + V_{\text{eff}}$ or $(l+I)(l+I+1)/y^2 + V'_{\text{eff}}$. The relative sizes of the two constituent pieces of the potential do not provide any clue, as they vary considerably with l . One way to tell the origin of the $I(l)$ factors would be to obtain the form of V_{eff} from a few assumptions about the nature of the electron-electron interactions that V_{eff} partially models.

In conclusion, the agreement obtained suggests that the analytical eigenvectors (11) may provide good trial wave

functions for detailed atomic calculations.⁹ The model may also serve as a phenomenological description that predicts certain previously unknown transition probabilities.

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