# On the Time-Independent Perturbation Theory

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The time-independent perturbation theory is developed for an arbitrary operator $\hat{H}(\lambda)=\sum_{k=0}^{\infty}\lambda^k\hat{H}^{(k)}$, which can be expanded in powers of the perturbation parameter $\lambda$. A unified formulation allows the establishment of a formal interrelation between the methods of Rayleigh-Schrödinger and of Brillouin-Wigner. We introduce a nonunitary transformation operator to connect the $n$th eigenket of $\hat{H}(0)$ with the $n$th eigenket of $\hat{H}(\lambda)$, and it is proven that this operator satisfies a Lippmann-Schwinger type equation. A perturbation method based on this equation is proposed, and it is applied to describe an electron moving in a Yukawa potential.

## 1. Introduction

The standard time-independent perturbation theory is usually based on the following assumptions [1–4]: (i) The Hamiltonian $\hat{H}(\lambda)$ is divided into a single unperturbed part $\hat{H}^{(0)}$ and a first-order perturbation operator $\lambda\hat{H}^{(1)}$; (ii) $\hat{H}^{(0)}$ and $\hat{H}^{(1)}$ are Hermitian operators; (iii) The perturbation parameter $\lambda$ is a small and real number.

In the present paper we fix our attention on an arbitrary operator $\hat{H}(\lambda)$ which depends of a parameter $\lambda$ and may be expanded into a power-series of $\lambda$ with contributions of any order,

$$\hat{H}(\lambda)=\sum_{k=0}^{\infty}\lambda^k\hat{H}^{(k)}=\hat{H}^{(0)}+\hat{V}(\lambda)\,, \tag{1}$$

where

$$\hat{V}(\lambda):=\sum_{k=1}^{\infty}\lambda^k\hat{H}^{(k)}\,. \tag{2}$$

For the moments, $\hat{H}(\lambda)$ and $\hat{H}^{(k)}$ $(k\geq 0)$ may be nonhermitian operators, and $\lambda$ may be a complex number.

The object of the present work is to present a unified treatment of time-independent perturbation theory and therefore to establish the formal interrelation existing between the methods of Rayleigh-Schrödinger [1], of Brillouin-Wigner [5] and of canonical transformations [3]. The core of the derivation is to allow perturbations of any order in the Rayleigh-Schrödinger theory. This permits a suitable generalization of the Rayleigh-Schrödinger formulae (Sect. 2, 3, 4) and their reorganization (Sect. 5, 6) in terms of the arbitrary full perturbation $\hat{V}(\lambda)$. It is also our purpose to unify the degenerate and nondegenerate cases in a common formal derivation of the time-independent perturbation theory. This is achieved by introducing a suitable projection operator $\hat{P}_n$, associated with the degenerate eigenvalue $E_n^{(o)}$ of the unperturbed operator $\hat{H}^{(0)}$.

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## 2. Fundamental Assumptions

The aim of the time-independent perturbation theory is to solve the eigenvalue equation

$$\hat{H}(\lambda)|\psi_n(\lambda)\rangle=E_n(\lambda)|\psi_n(\lambda)\rangle \tag{3}$$

associated with an arbitrary operator $\hat{H}(\lambda)$. To accomplish this, we start with the basic assumption of the Rayleigh-Schrödinger theory, according to which the operator $\hat{H}(\lambda)$, the eigenket $|\psi_n(\lambda)\rangle$ and the eigenvalue $E_n(\lambda)$ may be expanded in power series in the perturbation parameter $\lambda$:

$$\hat{H}(\lambda)=\sum_{k=0}^{\infty}\lambda^k\hat{H}^{(k)}\,, \tag{4}$$

$$E_n(\lambda)=\sum_{k=0}^{\infty}\lambda^k E_n^{(k)}\,, \tag{5}$$

$$|\psi_n(\lambda)\rangle=\sum_{k=0}^{\infty}\lambda^k|\psi_n^{(k)}\rangle\,. \tag{6}$$

In general, as $\hat{H}(\lambda)$ is known, the $k$th-order perturbation of the Hamiltonian is given by

$$\hat{H}^{(k)}:=\frac{1}{k!}\frac{\partial^k\hat{H}(\lambda)}{\partial\lambda^k}\Bigg]_{\lambda=0}\,. \tag{7}$$

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The entities $\hat{H}^{(0)}$, $E_n^{(0)}$ and $|\psi_n^{(0)}\rangle$ describe respectively the Hamiltonian, the energy and the eigenstate of the unperturbed system ($\lambda=0$). In our notation the subscript labels the state of the system, while the superscript refers to the order of the perturbation.

### 2.1 Normalization Condition

We require that the unperturbed eigenket be normalized to unity, $\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle=1$, and that the exact eigenket $|\psi_n(\lambda)\rangle$ be normalized according to the so-called intermediate normalization convention [6],

$$1=\langle\psi_n^{(0)}|\psi_n(\lambda)\rangle\,. \tag{8}$$

These conditions imply that the perturbed components of the eigenkets must be orthogonal to the original one, $|\psi_n^{(0)}\rangle$:

$$\langle\psi_n^{(0)}|\psi_n^{(m)}\rangle=\begin{cases}1 & \text{for } m=0\\ 0 & \text{for } m\geq 1\end{cases}. \tag{9}$$

Let us suppose that the unperturbed Hamiltonian $\hat{H}^{(0)}$ has a $g$-fold degenerate set of eigenkets $\{|\psi_{nr}^{(0)}\rangle$, $r=1,2,\ldots,g\}$, with common energy $E_n^{(o)}$. Then, the unperturbed eigenket $|\psi_n^{(0)}\rangle$ can be taken as a linear combination of the $g$-fold-degenerate eigenkets, namely:

$$|\psi_n^{(0)}\rangle=\sum_{r=1}^{g}a_r|\psi_{nr}^{(0)}\rangle,\quad \langle\psi_{nR}^{(0)}|\psi_{nr}^{(0)}\rangle=\delta_{Rr}, \tag{10}$$

where the coefficients are arbitrary – except by the normalization condition (9) – complex numbers. The $g$ eigenkets are generally not orthogonal, but they can always be transformed to an orthonormal set by a unitary transformation, as we have assumed in the last equation (10).

Now, we want to introduce a projection operator

$$\hat{P}_n=\hat{1}-\sum_{r=1}^{g}|\psi_{nr}^{(0)}\rangle\langle\psi_{nr}^{(0)}| \tag{11a}$$

which acts on an arbitrary ket and projects it onto the orthogonal complement of the subspace constructed with the eigenkets $|\psi_{nr}^{(0)}\rangle$,

$$|\Phi_n(\lambda)\rangle:=\hat{P}_n|\psi_n(\lambda)\rangle=\sum_{k=1}^{\infty}\lambda^k|\psi_n^{(k)}\rangle\,. \tag{11b}$$

In terms of the projection operator $\hat{P}_n$ we are able to realize the decomposition

$$|\psi_n(\lambda)\rangle=|\psi_n^{(0)}\rangle+\hat{P}_n|\psi_n(\lambda)\rangle\,. \tag{12}$$

### 2.2 Successive Approximations

Substituting (4), (5), and (6) in the eigenvalue equation (3), we obtain the expression

$$\sum_{k=0}^{\infty}\lambda^k(\hat{H}^{(k)}-E_n^{(k)})\sum_{l=0}^{\infty}\lambda^l|\psi_n^{(l)}\rangle=0\,. \tag{13}$$

We can rearrange this twofold sum by using the change of indices $m=k+l$, by assuming that the sum converges regardless of the order in which it is performed, and by collecting the coefficient of each power of $\lambda$ (see Appendix A):

$$\sum_{m=0}^{\infty}\lambda^m\sum_{k=0}^{m}(\hat{H}^{(k)}-E_n^{(k)})|\psi_n^{(m-k)}\rangle=0\,. \tag{14}$$

We require now that the coefficient of each power of $\lambda$ in this equation be individually zero, so that

$$\sum_{k=0}^{m}(\hat{H}^{(k)}-E_n^{(k)})|\psi_n^{(m-k)}\rangle=0,\quad \text{for } m=0,1,2,3,\ldots \tag{15}$$

In practice, we have to restrict the calculations to the $M$th order, i.e. we only take a finite set of equations, $m=0,1,2,3,\ldots,M$. The correction $|\psi_n^{(M)}\rangle$ includes all the corrections of lower order, so that the equations must be solved stepwise, starting with the unperturbed case ($m=0$):

$$\begin{aligned}&\lim_{\lambda\to 0}\hat{H}(\lambda)=\hat{H}^{(0)}=\hat{H}(0),\\ &\lim_{\lambda\to 0}E_n(\lambda)=E_n^{(0)}=E_n(0),\\ &\lim_{\lambda\to 0}|\psi_n(\lambda)\rangle=|\psi_n^{(0)}\rangle=|\psi_n(0)\rangle,\\ &(\hat{H}^{(0)}-E_n^{(0)})|\psi_n^{(0)}\rangle=0\,.\end{aligned} \tag{16}$$

From a formal point of view, it is very easy to express $|\psi_n^{(m)}\rangle$ in terms of the resolvent

$$\hat{G}^{(0)}(z):=(z-\hat{H}^{(0)})^{-1}=\frac{1}{z-\hat{H}^{(0)}}\,, \tag{17}$$

which is an operator that satisfies the identity

$$(z-\hat{H}^{(0)})\,\hat{G}^{(0)}(z)=\hat{G}^{(0)}(z)(z-\hat{H}^{(0)})=\hat{1}\,. \tag{18}$$

For later convenience we introduce the notation

$$\hat{G}_n^{(0)}:=\hat{G}^{(0)}(E_n^{(0)}+i\varepsilon), \tag{19}$$

$$\hat{G}_{n,\lambda}^{(0)}:=\hat{G}^{(0)}(E_n(\lambda)+i\varepsilon), \tag{20}$$

where the subscript $n$ refers to the $n$th eigenstate, and we assume that $\varepsilon$ is a very small, real and positive quantity.

If we separate in (15) the term $k=0$, we get an exact equation for $|\psi_n^{(m)}\rangle$,

$$|\psi_n^{(m)}\rangle = G_n^{(0)} \sum_{k=1}^{m} (\hat{H}^{(k)} - E_n^{(k)}) |\psi_n^{(m-k)}\rangle, \quad \text{for } m \geq 1.$$

Using the identity $|\psi_n^{(m)}\rangle = \hat{P}_n |\psi_n^{(m)}\rangle$, valid for $m \geq 1$, we get

$$|\psi_n^{(m)}\rangle = \hat{P}_n \sum_{k=1}^{m} \hat{G}_n^{[k]} |\psi_n^{(m-k)}\rangle, \quad \text{for } m \geq 1, \tag{21}$$

where we have introduced the notation

$$G_n^{[k]} := \hat{G}_n^{(0)} (\hat{H}^{(k)} - E_n^{(k)}), \quad \text{for } k \geq 1. \tag{22}$$

The introduction of the projector $\hat{P}_n$ in (21) is a basic step in the present paper. This operator will play an essential role in the perturbation treatment discussed below. On one hand it will guarantee the fulfillment of the orthogonality relations (9), throughout formal manipulations associated with a reorganization of the Rayleigh-Schrödinger expansions. On the other hand it will allow a unified treatment of the degenerate and nondegenerate cases of the time-independent perturbation theory.

## 3. Corrections to the Eigenvalues

To determine $\{E_n^{(0)}, E_n^{(1)}, E_n^{(2)}, \ldots\}$ we first take the scalar product of expression (3) with the bra $\langle\psi_n^{(0)}|$ and may thus write the eigenvalue $E_n(\lambda)$ as

$$\begin{aligned} E_n(\lambda) &= \langle\psi_n^{(0)}|\hat{H}(\lambda)|\psi_n(\lambda)\rangle \\ &= \sum_{m=0}^{\infty} \lambda^m \langle\psi_n^{(0)}|\hat{H}^{(m)}|\psi_n^{(0)}\rangle \\ &\quad + \sum_{k=0}^{\infty} \sum_{m=0}^{\infty} \lambda^{m+k} \langle\psi_n^{(0)}|\hat{H}^{(k)} \hat{P}_n |\psi_n^{(m)}\rangle, \end{aligned} \tag{23}$$

where the last line followed from using expansions (4) and (6). In particular, for the case of the unperturbed energy ($\lambda=0$), one has

$$E_n^{(0)} = \langle\psi_n^{(0)}|\hat{H}^{(0)}|\psi_n^{(0)}\rangle. \tag{24}$$

We now change the order of the double sum (see Appendix A), and by comparison with (5) we see that the corrections of the unperturbed energy are given by

$$\begin{aligned} E_n^{(m)} &= \langle\psi_n^{(0)}|\hat{H}^{(m)}|\psi_n^{(0)}\rangle \\ &\quad + \sum_{k=0}^{m} \langle\psi_n^{(0)}|\hat{H}^{(k)} \hat{P}_n |\psi_n^{(m-k)}\rangle. \end{aligned}$$

The term $k=m\geq 0$ does not contribute to the sum because $\hat{P}_n|\psi_n^{(0)}\rangle = 0$. For $m \geq 1$, the addend $k=0$ vanishes, even if $\hat{H}^{(0)}$ is a nonhermitian operator. To prove this we write the eigenvalue equation of $\hat{H}^{(0)}$ and its adjoint

$$\begin{aligned} &\hat{H}^{(0)}|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle, \\ &\langle\psi_n^{(0)}|(\hat{H}^{(0)})^+ = (E_n^{(0)})^* \langle\psi_n^{(0)}|. \end{aligned} \tag{25}$$

Now, by definition [7], the adjoint $\hat{A}^+$ of an operator $\hat{A}$ is defined by the relation $\langle \hat{A}^+ g|f\rangle = \langle g|\hat{A}f\rangle$, which is valid for all kets $|f\rangle$ and $|g\rangle$. In the present case, it is recognized that for $m \geq 1$

$$\begin{aligned} &\langle\psi_n^{(0)}|\hat{H}^{(0)}|\psi_n^{(m)}\rangle = \langle\psi_n^{(0)}|\hat{H}^{(0)}\psi_n^{(m)}\rangle \\ &= \langle(\hat{H}^{(0)})^+ \psi_n^{(0)}|\psi_n^{(m)}\rangle = (E_n^{(0)})^* \langle\psi_n^{(0)}|\psi_n^{(m)}\rangle = 0, \end{aligned} \tag{26}$$

where the last equality follows from the orthogonality relation (9).

In conclusion, the $m$th-order correction of the energy is determined by the relation

$$E_n^{(m)} = \sum_{k=1}^{m} \langle\psi_n^{(0)}|\hat{H}^{(k)} \hat{P}_n^{m-k} |\psi_n^{(m-k)}\rangle \quad \text{for } m \geq 1. \tag{27}$$

At this point, let us note that this relation only includes the first $m$ operators $\hat{H}^{(k)}$ ($1 \leq k \leq m$) instead of the full Hamiltonian $\hat{H}(\lambda)$. Also note that only the kets of order lower or equal to $(m-1)$ take part in the equation. To obtain (27) we have also used the identity

$$\hat{P}_n^k = \begin{cases} \hat{1} & \text{for } k=0 \\ \hat{P}_n & \text{for } k \geq 1 \end{cases}. \tag{28}$$

## 4. Rayleigh-Schrödinger Perturbation Theory

In the Rayleigh-Schrödinger (RS) method it is assumed that $\hat{H}^{(0)}$ represents an observable and that the complete set of unperturbed eigenkets $(\hat{H}^{(0)} - E_j^{(0)})|\psi_j^{(0)}\rangle = 0$ is known. Completeness is then given by the resolution of the identity operator

$$\hat{1} = \sum_j |\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|, \tag{29}$$

where the above expression includes a sum over the discrete spectrum plus an integral over the continuum of $\hat{H}^{(0)}$.

Substitution of (29) into (21) yields for the $m$th-correction to the eigenket

$$|\psi_n^{(m)}\rangle = \sum_{j \neq n} |\psi_j^{(0)}\rangle \frac{1}{E_n^{(0)} - E_j^{(0)}} C_{jn}^{(m)}, \quad \text{for } m \geq 1, \tag{30}$$

where the projector $\hat{P}_n$ was responsible for omitting the state (or states) with energy $E_n^{(0)}$. The coefficients of the

above expansion are given by

$$C_{jn}^{(m)} := \sum_{k=1}^{m} \langle \psi_j^{(0)} | \hat{H}^{(k)} | \psi_n^{(m-k)} \rangle . \tag{31}$$

Writing explicitly the contribution of $k=m$ in the above expression and using (30) allows us to express (31) as a recursion relation:

$$C_{jn}^{(m)} = \langle \psi_j^{(0)} | \hat{H}^{(m)} | \psi_n^{(0)} \rangle + \sum_{l \neq n} \frac{1}{E_n^{(0)} - E_l^{(0)}} \sum_{k=1}^{m-1} \cdot \langle \psi_j^{(0)} | \hat{H}^{(k)} | \psi_l^{(0)} \rangle C_{ln}^{(m-k)}, \tag{32}$$

where by convention the sum is identically zero if the upper limit is smaller than the lower one.

Similarly, the $m$th correction to the eigenvalue is obtained by writing explicitly the contribution of $k=m$ in sum (27) – using the identity $|\psi_n^{(m)}\rangle = \hat{P}_n |\psi_n^{(m)}\rangle$ for $m \geq 1$ – and by substituting (30) into (27). Hence we obtain the relation

$$\begin{aligned} E_n^{(m)} &= \langle \psi_n^{(0)} | \hat{H}^{(m)} | \psi_n^{(0)} \rangle + \sum_{k=1}^{m-1} \langle \psi_n^{(0)} | \hat{H}^{(k)} \hat{P}_n^{m-k} | \psi_n^{(m-k)} \rangle \\ &= \langle \psi_n^{(0)} | \hat{H}^{(m)} | \psi_n^{(0)} \rangle + \sum_{l \neq n} \frac{1}{E_n^{(0)} - E_l^{(0)}} \sum_{k=1}^{m-1} \cdot \langle \psi_n^{(0)} | \hat{H}^{(k)} | \psi_l^{(0)} \rangle C_{ln}^{(m-k)}, \\ E_n^{(m)} &= C_{nn}^{(m)} . \end{aligned} \tag{33}$$

There are no differences between the perturbation theory developed above and the conventional RS theory, except for the fact that some restrictions have been removed: $\hat{H}^{(m)}$ may be nonhermitian operators, perturbations $\hat{H}^{(m)}$ of the second order and higher have been taken into account, and limitation to the nondegenerate case has been dismissed. This method can also be related to other time-independent methods in a natural way, as will be done in the next sections.

## 5. Nonunitary Transformation Operator

Let us return to (21) and define an operator $\hat{U}_n^{(m)}$. When this operator acts on an unperturbed eigenstate $|\psi_n^{(0)}\rangle$, the result is the $m$th correction, according to the relation

$$|\psi_n^{(m)}\rangle = \hat{U}_n^{(m)} |\psi_n^{(0)}\rangle , \tag{34a}$$

with

$$\begin{aligned} \hat{U}_n^{(0)} &= \hat{1} , \\ \hat{U}_n^{(m)} &= \hat{P}_n \sum_{k=1}^{m} \hat{G}_n^{[k]} \hat{U}_n^{(m-k)} \quad \text{for } m \geq 1 \end{aligned} \tag{34b}$$

In agreement with the orthonormality relations (9), these operators satisfy

$$\langle \psi_n^{(0)} | \psi_n^{(m)} \rangle = \langle \psi_n^{(0)} | \hat{U}_n^{(m)} | \psi_n^{(0)} \rangle = \begin{cases} 1 & \text{for } m=0 \\ 0 & \text{for } m \geq 1 \end{cases} . \tag{35}$$

We can now use (6) to define an operator $\hat{U}_n(\lambda)$ that will transform the $n$th unperturbed eigenstate ($\lambda=0$) into the $n$th perturbed eigenstate of $\hat{H}(\lambda)$:

$$|\psi_n(\lambda)\rangle = \hat{U}_n(\lambda) |\psi_n^{(0)}\rangle , \tag{36a}$$

where

$$\hat{U}_n(\lambda) = \sum_{m=0}^{\infty} \lambda^m \hat{U}_n^{(m)} . \tag{36b}$$

Let us indicate that, if operator $\hat{U}_n(\lambda)$ were known, then the operators $\hat{U}_n^{(m)}$ could be determined by the relations

$$\hat{U}_n^{(m)} = \frac{1}{m!} \frac{\partial^m \hat{U}_n(\lambda)}{\partial \lambda^m} \Bigg]_{\lambda=0} . \tag{37}$$

The operator $\hat{U}_n(\lambda)$ – associated with the $n$th eigenstate – appears in a similar context as the one that Davidov described in his canonical transformation method [3]. In our case though, $\hat{U}_n(\lambda)$ cannot be assumed to be a unitary operator, since the properties of $\hat{U}_n(\lambda)$ are fixed by the definitions (34) and (36). Any further conditions imposed on $\hat{U}_n(\lambda)$ must be proved to be in accordance with those basic relations. The procedure developed in the present paper will be referred from now on as the *method of the transformation operator* $\hat{U}_n(\lambda)$.

### 5.1 *Lippmann-Schwinger Equation for the Perturbed Eigenstate*

Let us now demonstrate that the operator $\hat{U}_n(\lambda)$ satisfies an equation of the Lippmann-Schwinger type [8], which will allow us to establish the connection with the Brillouin-Wigner perturbation procedure [5].

By substitution of (34) in (36) we find that the operator $\hat{U}_n(\lambda)$ can be written as

$$\hat{U}_n(\lambda) = \hat{1} + \hat{P}_n \sum_{m=1}^{\infty} \lambda^m \sum_{k=1}^{m} \hat{G}_n^{[k]} \hat{U}_n^{(m-k)} . \tag{38}$$

By changing the order of the sums (Appendix A), we find

$$\hat{U}_n(\lambda) = \hat{1} + \hat{P}_n \hat{G}_n^{(0)} \hat{W}_n(\lambda) \hat{U}_n(\lambda) , \tag{39}$$

where we have used definition (22) for $G_n^{[k]}$ and have introduced a *relative perturbation*

$$\hat{W}_n(\lambda) := \sum_{k=1}^{\infty} \lambda^k (\hat{H}^{(k)} - E_n^{(k)}) = \hat{V}(\lambda) - (E_n(\lambda) - E_n^{(0)})$$
$$= (E_n^{(0)} - \hat{H}^{(0)}) - (E_n(\lambda) - \hat{H}(\lambda)). \quad (40)$$

Here $\hat{V}(\lambda)$ is the perturbation operator defined by (2). By combining (36a) and (39), we find that the solution of the eigenvalue equation satisfies the relation

$$|\psi_n(\lambda)\rangle = |\psi_n^{(0)}\rangle + \hat{P}_n \hat{G}_n^{(0)} \hat{W}_n(\lambda) |\psi_n(\lambda)\rangle, \quad (41)$$

which is an equation of the Lippmann-Schwinger type, as it is known from quantum collision theory [8]. The above equation is – as far as we are informed – a new result in the context of time-independent perturbation theory.

Equations (39) and (41) are solved by iteration, obtaining

$$\hat{U}_n(\lambda) = \hat{1} + \sum_{r=1}^{\infty} (\hat{P}_n \hat{G}_n^{(0)} \hat{W}_n(\lambda))^r, \quad (42)$$

$$|\psi_n(\lambda)\rangle = |\psi_n^{(0)}\rangle + \sum_{r=1}^{\infty} (\hat{P}_n \hat{G}_n^{(0)} \hat{W}_n(\lambda))^r |\psi_n^{(0)}\rangle, \quad (43)$$

where the subscript $n$ labels the $n$th eigenstate. Note that by substitution of (43) in (23) an implicit equation $E_n(\lambda) = F(E_n(\lambda))$ is obtained, which has the eigenvalue $E_n(\lambda)$ as solution

### *5.2 Consistency of the Results*

At this point it is valuable to verify the consistency of the results. In first place, we note that by substitution of the last part of the equality (40) in (41) and by using the identity (18) and eigenvalue equation (3) we obtain $|\psi_n(\lambda)\rangle = |\psi_n^{(0)}\rangle + \hat{P}_n |\psi_n(\lambda)\rangle$, which is in agreement with (12), as it should be.

We are able to prove that (43) is consistent with the starting equations (3) and (16) by applying the operator $(E_n^{(0)} - \hat{H}^{(0)} + i\varepsilon)$ to both sides of (41):

$$(E_n^{(0)} - \hat{H}^{(0)} + i\varepsilon) |\psi_n(\lambda)\rangle = (E_n^{(0)} - \hat{H}^{(0)} + i\varepsilon) |\psi_n^{(0)}\rangle$$
$$+ (E_n^{(0)} - \hat{H}^{(0)} + i\varepsilon) \hat{P}_n \hat{G}_n^{(0)} \hat{W}_n(\lambda) |\psi_n(\lambda)\rangle. \quad (44)$$

The first term of the right-side vanishes. By using the last equality of (40) to replace $\hat{W}_n(\lambda)$, the unperturbed equation $(\hat{H}^{(0)} - E_n^{(0)}) |\psi_n^{(0)}\rangle = 0$ is obtained. Finally, eigenvalue equation (3) for the full Hamiltonian can be reconstructed by using the identity

$$(E_n^{(0)} - \hat{H}^{(0)}) \hat{P}_n = E_n^{(0)} - \hat{H}^{(0)} \quad (45)$$

and relation (18).

## 6. Brillouin-Wigner Perturbation Theory

We will now demonstrate that the Brillouin-Wigner method (BW) emerges as a particular case of (41). To see how the BW procedure appears in the theory, let us restrict our considerations to a Hermitian operator $\hat{H}^{(0)}$. In this case, $\hat{H}^{(0)}$ and the projector $\hat{P}_n$ commute, and the following identity is valid:

$$(E_n^{(0)} - \hat{H}^{(0)} + i\varepsilon) \hat{P}_n = \hat{P}_n (E_n^{(0)} - \hat{H}^{(0)} + i\varepsilon),$$
$$\hat{H}^{(0)} \text{ Hermitian.} \quad (46)$$

By using this identity and (40), the relationship (44) can be rewritten as

$$[E_n(\lambda) - \hat{H}(\lambda) + i\varepsilon + (\hat{1} - \hat{P}_n) \hat{W}_n(\lambda)] |\psi_n(\lambda)\rangle$$
$$= [E_n(\lambda) - \hat{H}(\lambda) + i\varepsilon + (\hat{1} - \hat{P}_n) \hat{W}_n(\lambda)] |\psi_n^{(0)}\rangle$$
$$+ \hat{P}_n \hat{W}_n(\lambda) |\psi_n^{(0)}\rangle. \quad (47)$$

Taking into account (47), and the identity

$$E_n(\lambda) - \hat{H}(\lambda) + i\varepsilon + (\hat{1} - \hat{P}_n) \hat{W}_n(\lambda)$$
$$= (E_n(\lambda) - \hat{H}^{(0)} + i\varepsilon) \hat{P}_n - \hat{P}_n \hat{V}(\lambda), \quad (48)$$

we see that (47) implies the following equation for the perturbed eigenstate:

$$|\psi_n(\lambda)\rangle = |\psi_n^{(0)}\rangle + \hat{G}_n(\lambda) \hat{P}_n W(\lambda)_n(\lambda) |\psi_n^{(0)}\rangle, \quad (49)$$

where $\hat{G}_n(\lambda)$ is the *effective resolvent*

$$\hat{G}_n(\lambda) := \frac{1}{(E_n(\lambda) - \hat{H}^{(0)} + i\varepsilon) - \hat{P}_n \hat{V}(\lambda)}$$
$$= \sum_{r=0}^{\infty} (\hat{G}_{n,\lambda}^{(0)} \hat{P}_n \hat{V}(\lambda))^r \hat{G}_{n,\lambda}^{(0)}. \quad (50)$$

The last equality has been obtained by using the following identity in the limit as $N \to \infty$:

$$(\hat{A} - \hat{B})^{-1} = \hat{A}^{-1} + (\hat{A}^{-1} \hat{B})(\hat{A} - \hat{B})^{-1} \quad (51)$$
$$= \sum_{r=0}^{N-1} (\hat{A}^{-1} \hat{B})^r \hat{A}^{-1} + (\hat{A}^{-1} \hat{B})^N (\hat{A} - \hat{B})^{-1}.$$

Comparing (49) and (36a) we obtain

$$\hat{U}_n(\lambda) = \hat{1} + \hat{G}_n(\lambda) \hat{P}_n \hat{W}_n(\lambda) \quad (52)$$
$$= \hat{1} + \sum_{r=0}^{\infty} (\hat{G}_{n,\lambda}^{(0)} \hat{P}_n \hat{V}(\lambda))^r \hat{G}_{n,\lambda}^{(0)} \hat{P}_n [\hat{V}(\lambda) - (E_n(\lambda) - E_n^{(0)})],$$

where $\hat{G}_{n,\lambda}^{(0)}$ is the resolvent defined in (20).

We now apply this operator on the unperturbed eigenstate and use the relation $\hat{P}_n |\psi_n^{(0)}\rangle = 0$ to obtain

$$|\psi_n(\lambda)\rangle = |\psi_n^{(0)}\rangle + \sum_{r=1}^{\infty} (\hat{G}_{n,\lambda}^{(0)} \hat{P}_n \hat{V}(\lambda))^r |\psi_n^{(0)}\rangle. \quad (53)$$

This result can be rewritten as

$$|\psi_n(\lambda)\rangle = |\psi_n^{(0)}\rangle + \hat{G}^{(0)}_{n,\lambda}\,\hat{P}_n\,\hat{V}(\lambda)|\psi_n(\lambda)\rangle\,, \qquad \hat{H}^{(0)} \text{ Hermitian}, \tag{54}$$

which is the starting point of the *Brillouin-Wigner* method [5].

Note that the resolvent $\hat{G}^{(0)}_{n,\lambda}$ appears in the BW method, while the resolvent $\hat{G}^{(0)}_n$ emerges in the RS method and in the present transformation operator method – see general results (41) and (43) –. However, notwithstanding the simplicity of the resolvent $\hat{G}^{(0)}_n$, there is an implicit dependence of the unknown eigenvalue $E_n(\lambda)$ in (41) and (43).

## 7. Born and Brillouin-Wigner Approximations of Order *R*

So far, the equations obtained in the above sections are exact. Now we can use the expansions (43) and (53) to develop approximation methods. By definition, an approximation of order $R$ is the one that results of truncating sums (43) or (53) to the first $R$ terms. In the following we will speak of Born (B) approximation of order $R$ or of Brillouin-Wigner (BW) approximation of order $R$, depending on whether (43) or (53) respectively, is used.

In the subsequent development we will restrict our considerations to an Hermitian unperturbed operator $\hat{H}^{(0)}$, which represents an observable. By using the decomposition (29) for the unity operator, we find the first order B and BW approximations to the $n$th eigenstate:

$$|\overset{1}{\psi}{}^{B}_n\rangle = |\psi_n^{(0)}\rangle + \sum_{k\neq n} |\psi_k^{(0)}\rangle \frac{V_{kn}(\lambda)}{E_n^{(0)} - E_k^{(0)}}\,, \tag{55}$$

$$|\overset{1}{\psi}{}^{W}_n\rangle = |\psi_n^{(0)}\rangle + \sum_{k\neq n} |\psi_k^{(0)}\rangle \frac{V_{kn}(\lambda)}{\overset{1}{E}{}^{W}_n(\lambda) - E_k^{(0)}}\,. \tag{56}$$

The number one over the symbol $\psi$ labels the first order approximation, and the superscript (B or W) refers to Born and Brillouin-Wigner procedure, respectively. In the above equations we have introduced matrix elements

$$V_{nk}(\lambda) = \langle\psi_n^{(0)}|\,\hat{V}(\lambda)\,|\psi_k^{(0)}\rangle\,. \tag{57}$$

The above approximations are very similar to the one of Rayleigh-Schrödinger – see (30) –, but with some differences. In the RS approximation appears the first order perturbation $\hat{H}^{(1)}$, while in the B and W formulae emerges the full perturbation $\hat{V}(\lambda)$. Besides, (55) is calculated by using the unperturbed energies, while (56) involves the yet unknown eigenvalue $\overset{1}{E}{}^{W}_n(\lambda)$.

By using the above equations and (23), we find the first order Born and Brillouin-Wigner approximations for the eigenvalues of $\hat{H}(\lambda)$:

$$\overset{1}{E}{}^{B}_n(\lambda) = E_n^{(0)} + V_{nn}(\lambda) + \sum_{k\neq n} \frac{V_{nk}(\lambda)\,V_{kn}(\lambda)}{E_n^{(0)} - E_k^{(0)}}\,, \tag{58}$$

$$\overset{1}{E}{}^{W}_n(\lambda) = E_n^{(0)} + V_{nn}(\lambda) + \sum_{k\neq n} \frac{V_{nk}(\lambda)\,V_{kn}(\lambda)}{\overset{1}{E}{}^{W}_n(\lambda) - E_k^{(0)}}\,. \tag{59}$$

These two formulae are very similar except for the fact that the perturbed energy $\overset{1}{E}{}^{W}_n(\lambda)$ appears in the denominator of (59) instead of the unperturbed energy $E_n^{(0)}$. The first Born approximation is easier to use than the first BW procedure, because there is no necessity to solve an implicit equation for $\overset{1}{E}{}^{W}_n(\lambda)$.

The B and BW methods have good convergence properties compared to those of the RS perturbation theory. In the first order B and BW approximations, for example, appear contributions that only emerge in the second order RS procedure.

## 8. An Example: Yukawa Potential

In this section we consider as an example the Hamiltonian

$$\hat{H}(\lambda) = \frac{1}{2\mu}\,\hat{p}^2 - Z e^2 \frac{1}{r} \exp\left(-\lambda \frac{r}{a}\right) = \hat{H}^{(0)} + \hat{V}(\lambda), \tag{60}$$

$$\hat{H}^{(0)} = \frac{1}{2m}\,\hat{p}^2 - Z e^2 \frac{1}{r}\,, \tag{61}$$

$$\hat{V}(\lambda) = V(r,\lambda) = -Z\frac{a}{r}\left[\exp\left(-\lambda\frac{r}{a}\right) - 1\right]\varepsilon, \tag{62}$$

which describes an electron moving in a screened Coulomb (Yukawa) potential. This Hamiltonian has been used to study the energy levels of neutral atoms with nuclear charge $Z$ [9], using a screening parameter

$$\lambda = \lambda_0 Z^{1/3}\left(1 - \frac{1}{Z}\right)^{2/3}, \tag{63}$$

where $\lambda_0$ is taken to be $\lambda_0 = 0.98$. The following quantities will be used from now on: $m_e$ and $\mu_e$ are the mass and the reduced mass of the electron in presence of the nuclei of mass $M$, respectively, $e$ is the charge of the electron, $a_0$ is the unit of length, and $\varepsilon_0$ the unit of energy.

The unperturbed system ($\lambda=0$) is a hydrogen-like atom which has bound eigenfunctions that satisfy the eigenvalue equation

$$\hat{H}^{(0)}|n\,l\,m\rangle = E_n^{(0)}|n\,l\,m\rangle,$$

(because of the degeneration, $E^{(0)}_{n,l,m}=E_n^{(0)}$)

with

$$E_n^{(0)} = -\frac{1}{2}\frac{Z^2}{n^2}\varepsilon, \quad \varepsilon = \frac{\mu_e}{m_e}\varepsilon_0, \quad \varepsilon_0 = \frac{e^2}{a_0}, \quad a = \frac{m_e}{\mu_e}a_0,$$

where $(n, l, m)$ are quantum numbers, and $\varepsilon$ and $a$ are modified units of length and energy, respectively. The eigenstates of $\hat{H}^{(0)}$ are orthonormal,

$$\langle N\,L\,M|n\,l\,m\rangle = \delta_{Nn}\delta_{Ll}\delta_{Mm}.$$

### *8.1 First Born Approximation*

Our aim is to describe this system by applying the first-order Born approximation. Using the change of notation $n\to(n,l,m)$, we have

$$\hat{P}_{nlm} = \hat{1} - \sum_{l'=0}^{n-1}\sum_{m'=-l'}^{l'}|n\,l'\,m'\rangle\langle n\,l'\,m'|,$$

$$E^B_{nlm}(\lambda) = E^{(0)}_{nlm} + V_{nlm;\,nlm}(\lambda) + \sum_{N\neq n}\sum_{L}\sum_{M}\frac{V_{nlm;\,NLM}(\lambda)\,V_{NLM;\,nlm}(\lambda)}{E^{(0)}_{nlm}-E^{(0)}_{NLM}}, \quad (64)$$

where the matrix elements of the perturbation $\hat{V}(\lambda)$ – as defined by (57) – are given by

$$V_{NLM;\,nlm}(\lambda) = \langle N\,L\,M|\hat{V}(\lambda)|n\,l\,m\rangle = \Gamma_{NL;\,nl}(\lambda)\,\delta_{Ll}\,\delta_{Mm} \quad (65)$$

with the definition

$$\Gamma_{NL;\,nl}(\lambda) := \int_0^\infty r^2\,R_{NL}(\lambda)\,V(r,\lambda)\,R_{nl}(r)\,\mathrm{d}r. \quad (66)$$

For practical calculations, we note the relation

$$\Gamma_{NL;\,nl}(\lambda) = -Z\,a\,\varepsilon\,[\varrho_{NL;\,nl}(1,\lambda) - \varrho_{NL;\,nl}(1,0)], \quad (67)$$

where

$$\varrho_{NL;\,nl}(p,b) := \int_0^\infty r^p \exp\left(-b\frac{r}{a}\right) R_{NL}(r)\,R_{nl}(r)\,\mathrm{d}r, \quad (68)$$

$p$ is an integer greater than $-1$ and $b$ is a real parameter. Refer to appendix B for the calculation of this quantity.

In conclusion in the first-order Born approximation the energy is given by

$$E^B_{nlm}(\lambda) = E^{(0)}_{nlm} + \Gamma_{nl;\,nl}(\lambda) + \sum_{N\neq n}\frac{|\Gamma_{Nl;\,nl}(\lambda)|^2}{E^{(0)}_{nlm}-E^{(0)}_{Nlm}}, \quad (69)$$

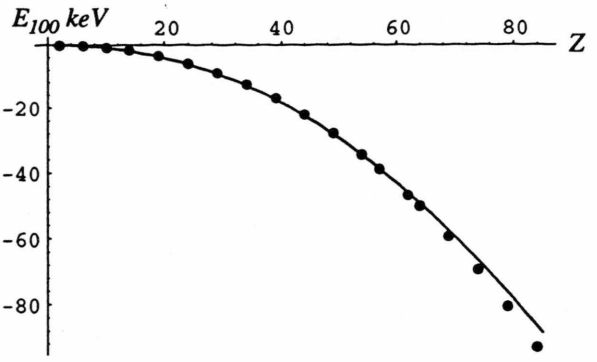


Fig. 1. Bound-state energy as a function of $Z$ for the state $(1,0,0)$. The solid line is the result of the first Born approximation by including in sum (69) the first ten values of the principal quantum number $N$. The points represent experimental data [10].

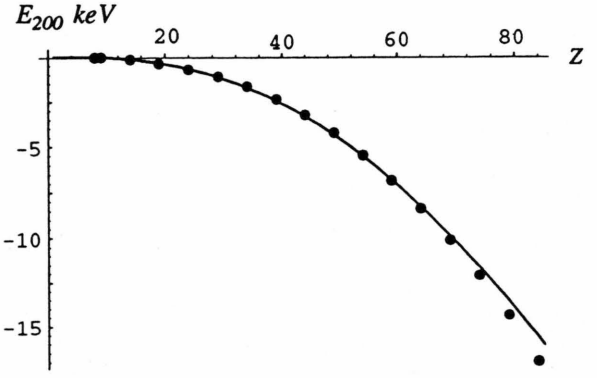


Fig. 2. Bound-state energy as a function of $Z$ for the state $(2,0,0)$. Solid line and points have the same meanings as in Figure 1.

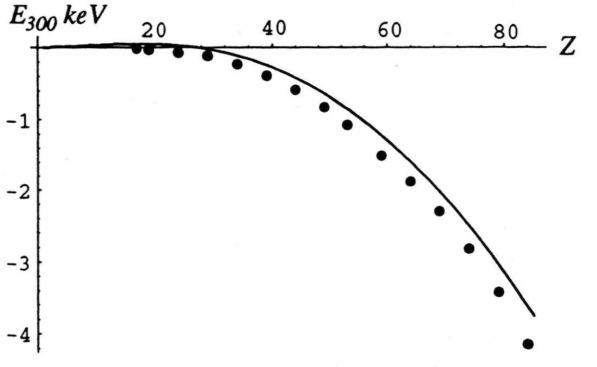


Fig. 3. Bound-state energies as a function of $Z$ for the state $(3,0,0)$. Solid line and points have the same meanings as in Figure 1.

where we have used the identity $V_{nlm;\,Nlm}(\lambda)=V_{Nlm;\,nlm}(\lambda)$ and the sum is over the principal quantum number, $N \neq n$.

### *8.2 Results within the First Born Approximation*

The Figs. 1, 2, and 3 show the results for the energies of neutral atoms corresponding to the states (1, 0, 0), (2, 0, 0) and (3, 0, 0). We have included in sum (69) only the first ten values of the quantum principal number $N$. The results are compared with the experimental values reported by Bearden and Burr [10]. Theory and experiment show an outstanding concordance for the K- and L-shell binding energies. There is a small deviation though, for our predictions for heavy atoms.

In the case of the state (3, 0, 0) the theoretical values exceed the experimental energy in the whole range of $Z$, and they also show an anomaly for low values of the atomic number $Z$ ($Z \leq 26$), since the calculated eigenvalues become positive. These facts indicate that the screening parameter $\lambda(Z)$ given by (63) is inadequate for higher values of the principal quantum number and that for excited states one should choose the screening parameter $\lambda_n(Z)$ that depends on $Z$ and on the principal quantum number $n$. In particular, if we set $\lambda_0=0.67$ for $Z=17$ and retain the functional dependence (63), we can approach the experimental value of $-0.0175\,\text{keV}$. However, this choice of $\lambda_0$ is unable to reproduce the experimental values of the energy for other values of $Z$.

## 9. Conclusion

In this paper we have formulated the time-independent perturbation theory in a general way, without restricting it to Hermitian operators or first-order perturbations. By appropriate formal manipulations, it has been possible to transform the Rayleigh-Schrödinger perturbation theory into the Brillouin-Wigner procedure. We have also develop a method directly related to the canonical transformations procedure of Davydov [3], introducing an operator $\hat{U}_n(\lambda)$ that connects the $n$th perturbed and the $n$th unperturbed eigenstate of the Hamiltonian $\hat{H}(\lambda)$. Unlike Davydov, we do not restrict $\hat{U}_n(\lambda)$ to be a unitary operator. The perturbed eigenstate satisfies a Lippmann-Schwinger type equation. Hence it has been possible to introduce an iterative method named Born approximation.

Unlike the method described in the presence paper, the older derivation of the BW method proceeded directly from the eigenvalue equation (3) without any reference to the Rayleigh-Schrödinger solution. We have shown that the Brillouin-Wigner method and the Born approximation are obtained as a consequence of the introduction of the projector $\hat{P}_n$ and by a suitable reordering of the Rayleigh-Schrödinger expansion.

In the standard Rayleigh-Schrödinger perturbation theory the nondegenerate and the degenerate cases in an unperturbed system must be treated separately. The results of the present paper are valid in both cases because of the introduction of the projector $\hat{P}_n$ and of the fact that the unperturbed eigenket $|\psi_n^{(0)}\rangle$ is a linear combination of $g$-fold-degenerate eigenkets. In particular, we may choose all coefficients in (10) as zero, except for one that must be chosen as one, in order to iterate the Lippmann-Schwinger equation by starting with the state $|\psi_n^{(0)}\rangle=|\psi_{nr}^{(0)}\rangle$.

We have applied as an example, the first Born approximation to study the energy levels of neutral atoms with nuclear charge $Z$, by using a Yukawa potential. The concordance of the theoretical and experimental results is excellent for $n=1$ and $n=2$, where $n$ is the principal quantum number. The discrepancies for $n=3$ are due to the choice of the screening parameter and are not related to the application of the first Born approximation.

At this point, it is worthwhile noting [11] that an expansion of the form

$$V(r,\lambda)=-\frac{a}{r}\sum_{k=1}^{\infty}V_k(\lambda r)^k$$

may be used to fit realistic numerical potentials such as the Hermann-Skillman or Hartree-Fock potentials, by choosing suitable coefficients $V_k$. The treatment developed in the present paper for the hydrogen-like potential requires only a few adaptations to be applied in this general case.

## Appendix A

Let us consider a set of (real or complex) numbers arrayed in the form

$$
\begin{array}{lllll}
A(N,M) & & & & \\
A(N+1,M) & A(N+1,M+1) & & & \\
A(N+2,M) & A(N+2,M+1) & A(N+2,M+2) & & \\
A(N+3,M) & A(N+3,M+1) & A(N+3,M+2) & A(N+3,M+3)\,. & \\
\ldots & \ldots & \ldots & \ldots & \ldots
\end{array}
$$

$A(n,m)$ is a function of two discrete variables, $n=N, N+1, N+2, N+3, \ldots, \infty$; $m=M+1, M+2, M+3, \ldots, \infty$, and $N$ and $M$ are predetermined integers.

By summation of these numbers, we obtain the identity

$$\sum_{n=N}^{\infty}\sum_{m=M}^{M-N+n} A(n,m)=\sum_{m=M}^{\infty}\sum_{n=N}^{\infty} A(n+m-M,m), \quad \text{(A1)}$$

where in one case we sum over columns and in the other over rows. We assume that the double sum converges, regardless of the order in which it is performed. Suitably renaming indices, this identity can be rewritten as

$$\sum_{k=K}^{\infty}\sum_{m=M}^{\infty} A(m+k-K,k)=\sum_{m=M}^{\infty}\sum_{k=K}^{K-M+m} A(m,k), \quad \text{(A2)}$$

where $K$ is a predetermined integer.

Now, it is possible to prove the equivalence of (13) and (14), which are fundamental in the present paper. By applying in (13) the change of indices $m=k+l$, with $k$ fixed, (13) becomes

$$\sum_{k=0}^{\infty}\sum_{m=k}^{\infty}\lambda^{m+k-k}(\hat{H}^{(k)}-E_n^{(k)})|\psi_n^{(m+k-2k)}\rangle=0, \quad \text{(A3)}$$

where, for convenience, we have written $l=m-k=m+k-2k$, $m=m+k-k$. Comparing (A3) and (A2) we identify that $K=0$, $M=k$ and

$$A(m+k-K,k)=\lambda^{m+k-k}(\hat{H}^{(k)}-E_n^{(k)})|\psi_n^{(m+k-2k)}\rangle.$$

Thus, (A3) may be expressed in the form

$$\sum_{m=k}^{\infty}\sum_{k=0}^{m-k}\lambda^{m-k}(\hat{H}^{(k)}-E_n^{(k)})|\psi_n^{(m-2k)}\rangle=0.$$

Finally, by introducing the change of indices $M=m-k$ with $k$ fixed, this equation may be rewritten as the desired equation (14).

## Appendix B

In this appendix we want to evaluate the quantity $\varrho_{NL;nl}(p,b)$, defined by (68), where $p$ is an integer greater than $-1$, and $b$ is a real parameter. To do this, we make use of the hydrogen-like radial wave functions,

$$R_{nl}(r)=N_{nl}\exp\left(-\frac{Z}{n}\frac{r}{a}\right)\cdot\left(2\frac{Z}{n}\frac{r}{a}\right)^{l}L_{n-l-1}^{2l+1}\left(2\frac{Z}{n}\frac{r}{a}\right), \quad \text{(B1)}$$

where the normalization coefficients $N_{nl}$ and the Laguerre polynomials $L_n^{\alpha}(x)$ are given by

$$N_{nl}=\left(\frac{2Z}{na}\right)^{3/2}\sqrt{\frac{(n-l-1)!}{2n(n+l)!}}, \quad \text{(B2)}$$

$$L_n^{\alpha}(x)=\sum_{k=0}^{n}D_n^{\alpha}(k)\,x^k, \quad \text{(B3)}$$

with

$$D_n^{\alpha}(k):=(-1)^k\frac{\Gamma(n+\alpha+1)}{\Gamma(k+\alpha+1)}\frac{1}{k!(n-k)!}. \quad \text{(B4)}$$

The above relations and the integral

$$\int_0^{\infty} r^n\exp(-\gamma r)\,\mathrm{d}r=\frac{\Gamma(n+1)}{\gamma^{n+1}}, \quad \text{for } n>-1 \quad \text{(B5)}$$

lead to

$$\varrho_{NL;nl}(p,b)=N_{NL}N_{nl}\left(2\frac{Z}{Na}\right)^{L}\left(2\frac{Z}{na}\right)^{l}\sum_{K=0}^{N-L-1}\sum_{k=0}^{n-l-1}\cdot D_{N-L-1}^{2L+1}(K)\,D_{n-l-1}^{2l+1}(k)\left(2\frac{Z}{Na}\right)^{K}\left(2\frac{Z}{na}\right)^{k}\cdot\frac{\Gamma(p+L+l+K+k+1)}{\gamma_{Nn}^{p+L+l+K+k+1}(b)}, \quad \text{(B6)}$$

where

$$\gamma_{Nn}(b):=\left(b+\frac{Z}{N}+\frac{Z}{n}\right)\frac{1}{a} \quad \text{(B7)}$$

is an auxiliary parameter.

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