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Two-particle coalescence conditions revisited

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ABSTRACT

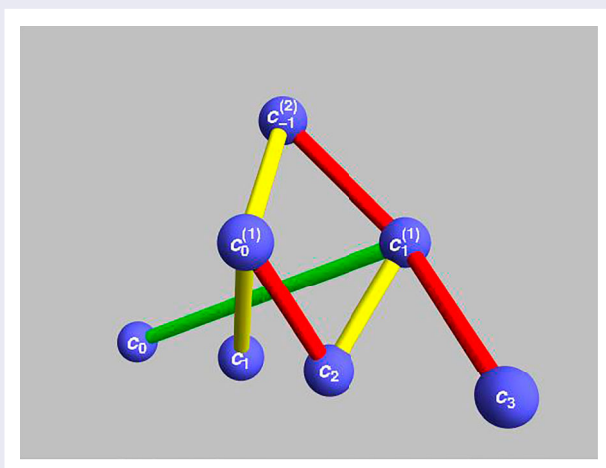
The notion of the n th order local energy, generated by the n th power of the Hamiltonian, has been introduced. The n th order two-particle coalescence conditions have been derived from the requirements that the n th order local energy at the coalescence point is non-singular and equal to the n th power of the Hamiltonian eigenvalue. The first condition leads to energy-independent constraints. The second one is state-specific. The analysis has been done using a radial, one-dimensional, model Hamiltonian. The model is valid in the asymptotic region of $r \sim 0$. The coalescence conditions set the relations between the expansion coefficients of the radial wave function into a power series with respect to r .

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1. Introduction

Two-particle Hamiltonians, since nearly a century, have been used as a playground for testing suitability of a variety of methods and models to the description of properties of simple quantum systems. The simplest ones, the hydrogen-like atom and the spherical harmonic oscillator not only served as a test of quantum mechanics, but also as a basis for the development of analytical methods of solving the Hamiltonian eigenvalue problem and for the studies on the properties of its spectrum. By a proper change of coordinates, a two-particle Hamiltonian can be expressed as a sum of two Hamiltonians:

one for the centre of mass and another one for the relative motion. Consequently, the resulting two-particle eigenvalue problem can be separated to two independent one-particle problems: one describing the free motion of the centre of mass and the second one, describing the relative motion of the two particles. In general, an external potential prevents the separability. An exception is the parabolic confinement. Two-particle Schrödinger equations, independent of the form of the interaction potential, are separable also in parabolic external potentials. The interaction potential V in the equation describing the relative motion depends only on the interparticle

distance $r_{12} \equiv r$. Therefore, the Hamiltonian commutes with the angular momentum operators and, after the elimination of the angular part, its eigenvalue problem transforms to an infinite set of eigenvalue equations

$$H \Phi_{v\lambda}(r) = E_{v\lambda} \Phi_{v\lambda}(r) \quad (1)$$

of one-dimensional radial Hamiltonians

$$H = -\frac{1}{2\mu} \frac{d^2}{dr^2} + \frac{\lambda(\lambda+1)}{2\mu r^2} + V(r), \quad (2)$$

where $\lambda = 0, 1, 2, \dots$ is the angular momentum quantum number and μ is the reduced mass.¹ In the case of two identical fermions the wave function is symmetric (a singlet pair) if λ is even and antisymmetric (triplet) if λ is odd.

The point $r = 0$ corresponds to the coalescence of the two particles. The information about the behaviour of the exact wave functions at this point is important both for the understanding of general properties of many-particle systems and for the construction of variational trial functions. Therefore, the subject attracted much interest – see, e.g. [1–14] and references therein. Hamiltonian (2) offers a simple and easy to treat model. Though this model describes a ‘bare’ pair of particles, under certain assumptions it can be generalised so that, after some modifications, it can be also applied to studies on the coalescence conditions in N -particle systems. In particular, if the distance r between two coalescing particles is much smaller than the distance to any of the remaining $N-2$ particles, then one may expect that the influence of these particles on the properties of the coalescing pair can be described by a two-particle effective potential, parametrically dependent on the coordinates of the other particles. After an approximate separation of the centre of mass of the two particles and a spherical averaging, we end up with a radial equation describing the pair of particles in the vicinity of the coalescence point. From here one can derive constraints on the asymptotic form of the exact wave functions at the limit of $r = 0$. The best known of these constraints, Kato’s cusp condition [1], can be derived from the requirement that in the case of two Coulomb-interacting particles the local energy is non-singular at $r = 0$. Higher-order coalescence constraints have been obtained using some other universal properties of the exact wave functions in the vicinity of $r = 0$ [2–5]. In a similar way the effects of the electron–electron coalescence on the electron density can be investigated. The earliest works on this subject were published already half a century ago [6], but the links with the structure of the first-order density matrix and of the natural orbitals have been discovered very recently [7–9]. A detailed analysis of the wave function coalescence constraints, referred

to as *general coalescence conditions for the exact wave functions*, has been given by Kurokawa *et al.* [10–12].

A sensitive tool for the exploration of the behaviour of $\Phi_{v\lambda}(r)$ at $r = 0$ is the local energy. Let $\Psi_{v\lambda}(r)$ be a trial function which for specific values of parameters, and for $r \ll 1$, is equal to $\Phi_{v\lambda}(r)$. We define the n th order local energy as

$$\frac{H^n \Psi_{v\lambda}(r)}{\Psi_{v\lambda}(r)} = \mathcal{E}_{v\lambda}^{(n)}(r). \quad n = 1, 2, 3, \dots \quad (3)$$

If $\Psi_{v\lambda}(r) = \Phi_{v\lambda}(r)$, i.e. it is the exact eigenfunction of H , then $\mathcal{E}_{v\lambda}^{(n)}(r) = E_{v\lambda}^n$. In this paper we derive the general two-particle coalescence conditions, as the ones of Kurokawa *et al.* [10–12], from the properties of the local energies at $r = 0$.² We perform the analysis for a separable, model in which the radial part of the interaction is described by Hamiltonian (2). The constraints are derived using the information about the behaviour of the wave function at $r = 0$. Therefore, the results are valid for both discrete and continuous spectra.

For eigenfunctions of Hamiltonian (2) the local energies of all orders have to be non-singular at the coalescence point. This property implies that the wave function has to compensate $r = 0$ singularities generated by the Hamiltonian. The constraints imposed by the enforcement of this property are, for a given λ , energy-independent, i.e. they are common to all wave functions $\Psi_{v\lambda}(r)$ which belong to the space spanned by the eigenfunctions of the radial Hamiltonian (2). In the case of Coulomb-interacting particles and $n = 1$ this constraint leads to Kato’s cusp condition [1].

If at the coalescence point $\Psi_{v\lambda}(r)$ behaves as an eigenfunction of H corresponding to the eigenvalue $E_{v\lambda}$ then

$$\mathcal{E}_{v\lambda}^{(n)}(r) |_{r=0} = E_{v\lambda}^n. \quad (4)$$

This property is, by definition, energy-dependent. Therefore, the constraints imposed by its enforcement are state-specific.

In the next section general coalescence conditions are derived and in Section 3 an example of application is given. A graphical method of deriving explicit form of the energy-independent coalescence conditions is presented in the Appendix. Atomic units are used in this paper.

2. Coalescence constraints

If we assume a Coulomb-like behaviour of $V(r)$ at $r = 0$, expand it to a power series about this point, and retain the first $q + 2$ terms of the expansion then we get

$$V(r) = \sum_{p=-1}^q \alpha_p r^p, \quad (5)$$

where, in the case of a parabolic confinement, α_2 contains a contribution from the external potential. For Coulombic systems and for $r \ll 1$, the term corresponding to $p = -1$ is dominant and determines the physical character of the potential. If $\alpha_{-1} > 0$ then the potential is repulsive (describing, for example, the interaction between two electrons); if $\alpha_{-1} < 0$, it can describe an attractive electron–nucleus interaction. Formally, the potential parameters are unrestricted. If $\alpha_{-1} = 0$, then the potential loses its Coulombic character but, nevertheless, the higher-order coalescence conditions impose wave function constraints dependent on α_p with $p > 0$ (cf. Section 2.1.2).³ The higher-order terms in Equation (5) improve the analytic representation of the potential in the vicinity of the coalescence point, but have no physical meaning for large values of r . For example, a term $\alpha_q r^q$, $\alpha_q > 0$, $q \geq 1$, prevents any kind of dissociation of the two particles.

For $r \sim 0$ the radial functions describing the coalescing pair can be expressed as

$$\Psi_{\nu\lambda}(r) \sim r^{\lambda+1} \psi_{\nu\lambda}(r), \quad \psi_{\nu\lambda}(0) \neq 0, \quad (6)$$

where ν refers to the energy eigenvalue and prefactor $r^{\lambda+1}$ compensates the singularity at $r \rightarrow 0$ generated by the centrifugal potential $\lambda(\lambda+1)/r^2$ [16]. As the normalisation condition we set $\psi_{\nu\lambda}(0) = 1$. Since $\Psi_{\nu\lambda}(r)$ is analytic [15] it can be expanded to a power series of r . We assume that $\psi_{\nu\lambda}(r)$ has an asymptotic expansion of order s about $r = 0$:

$$\psi_{\nu\lambda}(r) \sim \sum_{i=0}^s c_i r^i \quad (7)$$

(to simplify notation, indices ν and λ in c_i are omitted). For $r \ll 1$, Equations (6) and (7), with properly defined expansion coefficients, give a correct representation of the eigenfunctions of H at the vicinity of the coalescence point. Note that $\Psi_{\nu\lambda}(r)$ provides an asymptotic form of the corresponding eigenfunction but has no physical meaning outside of the coalescence region. First, the model is physically meaningful only for small r . Second, $\Psi_{\nu\lambda}(r)$, as defined in Equation (6), is not square-integrable in the range $r \in (0, \infty)$.

Our aim is to derive the conditions limiting the values of the coefficients of expansion (7) from two requirements defining the behaviour of $\mathcal{E}_{\nu\lambda}^{(n)}(r)$ at $r = 0$. The first group of these conditions, referred to as the *energy-independent constraints*, is a consequence of the requirement that $\mathcal{E}_{\nu\lambda}^{(n)}(r)$ is non-singular at $r = 0$. The second group, the *energy-dependent constraints*, follows from the condition given by Equation (4). Since we are interested in the properties of the local energies at $r = 0$, the behaviour of the wave functions outside of the asymptotic region is irrelevant for this discussion.

2.1. Energy-independent constraints

We set

$$\Psi_{\nu\lambda}^{(0)}(r) = r^{\lambda+1} \psi_{\nu\lambda}^{(0)}(r), \quad (8)$$

where

$$\psi_{\nu\lambda}^{(0)}(r) = \sum_{i=0}^s c_i^{(0)} r^i, \quad c_i^{(0)} = c_i, \quad (9)$$

and c_i is defined in Equation (7). Hereafter, superscript (0) in c_i is usually dropped out. According to Equations (2) and (5)

$$H r^{\lambda+1+i} = r^{\lambda+1} \left(A_i r^{i-2} + \sum_{p=-1}^q \alpha_p r^{p+i} \right), \quad (10)$$

where

$$A_i = -\frac{i(2\lambda + i + 1)}{2\mu}. \quad (11)$$

The combination of Equations (8) and (10) yields

$$H \Psi_{\nu\lambda}^{(0)}(r) = r^{\lambda+1} \left(\frac{c_{-1}^{(1)}}{r} + \psi_{\nu\lambda}^{(1)}(r) \right), \quad (12)$$

where

$$\psi_{\nu\lambda}^{(1)}(r) = \sum_{i=0}^{s+q} c_i^{(1)} r^i, \quad (13)$$

$$c_i^{(1)} = \sum_{p=-1}^q \alpha_p c_{i-p}^{(0)} + A_{i+2} c_{i+2}^{(0)}, \quad (14)$$

$$i = -1, 0, 1, \dots, s+q,$$

$$\text{with } c_k^{(0)} = 0, \quad \text{if } k < 0, \text{ or } k > s.$$

According to Equations (3), (8) and (12).

$$\mathcal{E}_{\nu\lambda}^{(1)}(r) = \frac{H \Psi_{\nu\lambda}^{(0)}(r)}{\Psi_{\nu\lambda}^{(0)}(r)} = \left(\frac{c_{-1}^{(1)}}{r} + \psi_{\nu\lambda}^{(1)}(r) \right) \frac{1}{\psi_{\nu\lambda}^{(0)}(r)}. \quad (15)$$

Since $\lim_{r \rightarrow 0} \psi_{\nu\lambda}^{(0)}(r) = c_0^{(0)} = 1$, and $\lim_{r \rightarrow 0} \psi_{\nu\lambda}^{(1)}(r) = c_0^{(1)}$, the first-order local energy is asymptotically, at $r \sim 0$, equal to

$$\mathcal{E}_{\nu\lambda}^{(1)}(r) \underset{r \rightarrow 0}{\sim} \frac{c_{-1}^{(1)}}{r} + c_0^{(1)}, \quad (16)$$

where, according to Equation (14),

$$\begin{aligned} c_{-1}^{(1)} &= \alpha_{-1} c_0^{(0)} + A_1 c_1^{(0)}, \\ c_0^{(1)} &= \alpha_{-1} c_1^{(0)} + \alpha_0 c_0^{(0)} + A_2 c_2^{(0)}. \end{aligned} \quad (17)$$

As it follows from Equation (16), $\mathcal{E}_{v\lambda}^{(1)}(0)$ is finite if $c_{-1}^{(1)} = 0$. Therefore, the first-order coalescence constraint reads

$$c_1^{(0)} = -\frac{\alpha_{-1}}{A_1} c_0^{(0)}. \quad (18)$$

If $c_{-1}^{(1)} = 0$ then

$$H\Psi_{v\lambda}^{(0)}(r) = r^{\lambda+1} \psi_{v\lambda}^{(1)}(r) \equiv \Psi_{v\lambda}^{(1)}(r), \quad (19)$$

and the procedure described by Equations (9)–(18) may be repeated with superscripts (0) and (1) replaced, respectively, by (1) and (2).

In general, if

$$c_{-1}^{(j)} = \alpha_{-1} c_0^{(j-1)} + A_1 c_1^{(j-1)} = 0, \quad \text{for } j = 1, 2, \dots, n-1, \quad (20)$$

where

$$c_i^{(j)} = \sum_{p=-1}^q \alpha_p c_{i-p}^{(j-1)} + A_{i+2} c_{i+2}^{(j-1)},$$

$$i = -1, 0, 1, \dots, s+jq,$$

$$\text{with } c_k^{(j-1)} = 0, \quad \text{if } k < 0, \text{ or } k > s + (j-1)q, \quad (21)$$

then

$$H\Psi_{v\lambda}^{(j-1)}(r) = r^{\lambda+1} \psi_{v\lambda}^{(j)}(r) \equiv \Psi_{v\lambda}^{(j)}(r), \quad (22)$$

and

$$\mathcal{E}_{v\lambda}^{(n)}(r) \underset{r \rightarrow 0}{\sim} \frac{c_{-1}^{(n)}}{r} + c_0^{(n)}, \quad (23)$$

where

$$\begin{aligned} c_{-1}^{(n)} &= \alpha_{-1} c_0^{(n-1)} + A_1 c_1^{(n-1)}, \\ c_0^{(n)} &= \alpha_{-1} c_1^{(n-1)} + \alpha_0 c_0^{(n-1)} + A_2 c_2^{(n-1)}. \end{aligned} \quad (24)$$

From here we have

Theorem 2.1: *The n th order local energy $\mathcal{E}_{v\lambda}^{(n)}(r)$ is finite at $r = 0$ if $c_{-1}^{(j)} = 0$ for $j = 0, 1, 2, \dots, n$.*

Corollary: *The coalescence constraints are independent of the free parameter, α_0 , in the potential.*

Proof: $c_{-1}^{(1)}$ [Equation (17)] does not depend on α_0 . Assume that $c_{-1}^{(j)}$, $j = 1, 2, \dots, n-1$, do not depend on

α_0 . Then

$$\begin{aligned} c_{-1}^{(n)} &= \alpha_{-1} c_0^{(n-1)} + A_1 c_1^{(n-1)} \\ &= \alpha_0 \left[\alpha_{-1} c_0^{(n-2)} + A_1 c_1^{(n-2)} \right] \\ &\quad + \alpha_{-1} \left[\alpha_{-1} c_1^{(n-2)} + (A_1 + A_2) c_2^{(n-2)} \right] \\ &\quad + A_1 \left[\alpha_1 c_0^{(n-2)} + A_3 c_3^{(n-2)} \right]. \end{aligned} \quad (25)$$

According to Theorem 2.1, $\alpha_{-1} c_0^{(n-2)} + A_1 c_1^{(n-2)} = c_{-1}^{(n-1)} = 0$. Therefore, $c_{-1}^{(n)}$ does not depend on α_0 . ■

Since $E_{v\lambda}$ can be included to α_0 , the Corollary implies that the coalescence conditions derived from the requirement that the n th order local energies are non-singular at $r = 0$ are, as expected, independent of the energy eigenvalues.

The coefficient $c_{-1}^{(1)}$ is a linear combination of $c_0^{(0)}$ and $c_1^{(0)}$ [Equation (17)]. Similarly, $c_{-1}^{(2)}$ is a combination of $c_0^{(1)}$ and $c_1^{(1)}$, i.e. of $c_j^{(0)}$, with $j = 0, 1, 2, 3$. As one can deduce from Equation (21), in order to obtain $c_{-1}^{(n)}$, one needs $c_j^{(0)}$ with $j = 0, 1, \dots, 2n-1$. Therefore, the minimum value of s in Equation (7) is $2n-1$. In practical terms, the upper limit for the highest order coalescence constraint is set by this condition – the coefficients of high powers of r are ill defined in the asymptotic region because $r \ll 1$ implies that the high powers of r are very small. Hereafter we set

$$s = 2n - 1.$$

Theorem 2.1 with Equations (20) and (21) yields explicit expressions for the energy-independent coalescence constraints:

$$c_{-1}^{(n)} = \sum_{i=0}^{2n-1} t_{ni} c_i = 0, \quad (26)$$

where

$$\begin{aligned} t_{10} &= \alpha_{-1}, & t_{11} &= A_1, \\ t_{20} &= \alpha_1 A_1, & t_{21} &= \alpha_{-1}^2, \\ t_{22} &= \alpha_{-1} (A_1 + A_2), & t_{23} &= A_1 A_3, \\ t_{30} &= \alpha_{-1}^2 \alpha_1 + \alpha_{-1} \alpha_2 (A_1 + A_2) + \alpha_3 A_1 A_3, \\ t_{31} &= \alpha_{-1} \alpha_1 (2A_1 + A_2) + \alpha_2 A_1 A_3, \\ t_{32} &= \alpha_{-1}^3 + \alpha_1 A_1 (A_2 + A_3), \\ t_{33} &= \alpha_{-1}^2 (A_1 + A_2 + A_3), \\ t_{34} &= \alpha_{-1} (A_1 A_3 + A_1 A_4 + A_2 A_4), & t_{35} &= A_1 A_3 A_5, \dots \end{aligned}$$

A graphical method of deriving t_{mi} coefficients is presented in the Appendix. From the first-order ($n = 1$)

constraint one can get the well-known cusp condition generated by the Coulomb singularity:

$$c_1 = -\frac{\alpha_{-1}}{A_1} c_0 = \frac{\alpha_{-1} \mu}{\lambda + 1} c_0. \quad (27)$$

This condition defines the coefficient of the linear term of the expansion of the radial function. In the case of two-electron coalescence it is equivalent to Kato's cusp condition [1]. For $n = 2$ we get, additionally, the second-order constraint:

$$-A_1 A_3 c_3 = \alpha_{-1} A_1 c_0 + \alpha_{-1}^2 c_1 + \alpha_{-1} (A_1 + A_2) c_2, \quad (28)$$

where c_1 can be eliminated using Equation (27). In energy-independent constraints the *odd* coefficients, $c_1, c_3, c_5, \dots$, can be expressed as linear functions of the *even* ones, $c_0, c_2, c_4, \dots$:

$$\begin{aligned} c_1 &= D_0^{(1)} c_0, \\ c_3 &= D_0^{(2)} c_0 + D_2^{(2)} c_2, \\ c_5 &= D_0^{(3)} c_0 + D_2^{(3)} c_2 + D_4^{(3)} c_4, \\ &\dots \quad \dots \quad \dots \quad \dots \end{aligned} \quad (29)$$

where

$$\begin{aligned} D_0^{(1)} &= -\frac{\alpha_{-1}}{A_1}, \quad D_0^{(2)} = \frac{\alpha_{-1}^3}{A_1^2 A_3} - \frac{\alpha_{-1}}{A_3}, \\ D_2^{(2)} &= -\frac{\alpha_{-1} (A_1 + A_2)}{A_1 A_3}, \quad \dots \end{aligned} \quad (30)$$

In general,

$$c_{2i+1} = \sum_{j=0}^i D_{2j}^{(i+1)} c_{2j}, \quad i = 0, 1, \dots, n-1. \quad (31)$$

The asymptotic expansion of the wave function [Equation (9)] becomes

$$\psi_{v\lambda}^{(0)}(r) = \sum_{i=0}^{n-1} \left(c_{2i} + r \sum_{j=0}^i D_{2j}^{(i+1)} c_{2j} \right) r^{2i}, \quad (32)$$

where we set $s = 2n-1$. Alternatively, we can arrange the expansion according to the *even* coefficients:

$$\psi_{v\lambda}^{(0)}(r) = \sum_{i=0}^{n-1} c_{2i} W^{(2i)}(r) r^{2i}, \quad (33)$$

where

$$W^{(2i)}(r) = 1 + \sum_{j=i+1}^n D_{2i}^{(j)} r^{2j-1}. \quad (34)$$

The local energy $\mathcal{E}^{(n)}$ does not diverge at $r = 0$, regardless of the values of c_{2j} , $j = 0, 1, 2, \dots, n-1$, if the

odd expansion coefficients, c_{2j+1} , are defined as in Equation (31). As a consequence, the terms $c_{2i} r^{2i}$ in the expansion of the wave function are multiplied by polynomials $W^{(2i)}(r)$, containing only odd powers of r , with coefficients defined by the Hamiltonian parameters.

2.1.1. Pure Coulomb potential

In the pure Coulomb case, i.e. if $\alpha_p = 0$ for $p \neq -1$, Equation (21) simplifies to

$$c_i^{(j)} = \alpha_{-1} c_{i+1}^{(j-1)} + A_{i+2} c_{i+2}^{(j-1)}. \quad (35)$$

Then,

$$\begin{aligned} c_{-1}^{(n)} &= \alpha_{-1} c_0^{(n-1)} + A_1 c_1^{(n-1)} \\ &= \alpha_{-1} \left[\alpha_{-1} c_1^{(n-2)} + A_2 c_2^{(n-2)} \right] \\ &\quad + A_1 \left[\alpha_{-1} c_2^{(n-2)} + A_3 c_3^{(n-2)} \right] \\ &= \alpha_{-1}^2 c_1^{(n-2)} + \alpha_{-1} (A_1 + A_2) c_2^{(n-2)} + A_1 A_3 c_3^{(n-2)} \\ &= \dots \quad \dots \quad \dots \\ &= \sum_{p=0}^j \alpha_{-1}^{n-j} \mathcal{A}_p^{(j)} c_{j+p-1}^{(n-j)} = \dots \\ &= \sum_{p=0}^n \alpha_{-1}^{n-p} \mathcal{A}_p^{(n)} c_{n+p-1}, \end{aligned} \quad (36)$$

where $\mathcal{A}_p^{(j)}$ is a $\binom{j}{p}$ -term combination of p -fold products of A_i . In particular, $\mathcal{A}_0^{(n)} = 1$, $\mathcal{A}_1^{(n)} = \sum_{i=1}^n A_i$, $\mathcal{A}_n^{(n)} = \prod_{i=1}^n A_{2i-1}$, $\mathcal{A}_2^{(3)} = A_1 A_3 + A_1 A_4 + A_2 A_4$, $\mathcal{A}_2^{(4)} = \mathcal{A}_2^{(3)} + A_5 (A_1 + A_2 + A_3)$, $\mathcal{A}_3^{(4)} = A_1 A_3 A_5 + A_1 A_3 A_6 + A_1 A_4 A_6 + A_2 A_4 A_6$, A graphical method of the evaluation of $\mathcal{A}_p^{(n)}$ is given in the Appendix.

For $n = 4$ the constraints for the pure Coulomb potential read

$$\begin{aligned} c_{-1}^{(1)} &= \alpha_{-1} c_0 + A_1 c_1 = 0, \\ c_{-1}^{(2)} &= \alpha_{-1}^2 c_1 + \alpha_{-1} (A_1 + A_2) c_2 + A_1 A_3 c_3 = 0, \\ c_{-1}^{(3)} &= \alpha_{-1}^3 c_2 + \alpha_{-1}^2 (A_1 + A_2 + A_3) c_3 \\ &\quad + \alpha_{-1} (A_1 A_3 + A_2 A_4 + A_1 A_4) c_4 \\ &\quad + A_1 A_3 A_5 c_5 = 0, \\ c_{-1}^{(4)} &= \alpha_{-1}^4 c_3 + \alpha_{-1}^3 (A_1 + A_2 + A_3 + A_4) c_4 \\ &\quad + \alpha_{-1}^2 (A_1 A_3 + A_2 A_4 + A_1 A_4 \\ &\quad + A_1 A_5 + A_3 A_5 + A_2 A_5) c_5 \\ &\quad + \alpha_{-1} (A_1 A_3 A_5 + A_1 A_3 A_6 + A_1 A_4 A_6 \\ &\quad + A_2 A_4 A_6) c_6 + A_1 A_3 A_5 A_7 c_7 = 0. \end{aligned} \quad (37)$$

2.1.2. Potentials non-singular at $r = 0$

Though potential (5) with $\alpha_{-1} = 0$ has no singularity at $r = 0$, it also generates singularities of higher-order local energies and coalescence constraints similar to the ones obtained for the singular potential. As it follows from Equation (24), if $\alpha_{-1} = 0$ then $c_1^{(n)} = 0$. The remaining odd coefficients do not vanish. According to Equation (21), $c_1^{(1)} = \alpha_1 c_0 + A_2 c_3$. As it was shown above, $c_1^{(1)} = 0$. Therefore, $A_3 c_3 = -\alpha_1 c_0$, i.e. $c_3 \neq 0$ unless $\alpha_1 = 0$. If $\alpha_{-1} = \alpha_1 = 0$, then $c_1 = c_3 = 0$, but $A_5 c_5 = -\alpha_3 c_0$, and so on. Using Equation (21) one can prove by induction

Theorem 2.2: *If $\alpha_{2p-1} = 0$ for $p = 0, 1, 2, \dots, m$, then $c_{2p+1}^{(0)} = 0$ for $p = 0, 1, 2, \dots, m$.*

Corollary: *If $V(r)$ contains only even powers of r , then*

$$\psi^{(0)}(r) = \sum_{i=0}^{n-1} c_{2i}^{(0)} r^{2i}. \quad (38)$$

2.2. Energy-dependent coalescence constraints

The coalescence constraints considered so far depend on the angular momentum of the coalescing pair but do not depend on the energy eigenvalue. The constraints, expressed as linear relations between coefficients c_i of the asymptotic expansions of the radial functions, are the same for all eigenfunctions of H . Therefore, they have to be fulfilled also by the linear combinations of the eigenfunctions.

We assume that the energy-independent constraints are fulfilled. Consequently, the local energies of all orders from 1 to n are non-singular at $r = 0$. The energy-dependent constraints result from the application of condition (4). It is convenient to include α_0 – the free parameter in the potential – to the eigenvalue. We define

$$\tilde{H} = H - \alpha_0, \quad \epsilon = E_{\nu\lambda} - \alpha_0, \quad (39)$$

and

$$\begin{aligned} \tilde{\mathcal{E}}_{\nu\lambda}^{(n)}(r) &= \frac{\tilde{H}^n \Psi_{\nu\lambda}(r)}{\Psi_{\nu\lambda}(r)} = \frac{(H - \alpha_0)^n \Psi_{\nu\lambda}(r)}{\Psi_{\nu\lambda}(r)} \\ &= \sum_{j=0}^n (-1)^{n-j} \binom{n}{j} \alpha_0^{n-j} \mathcal{E}_{\nu\lambda}^{(j)}(r), \end{aligned} \quad (40)$$

where, to simplify notation, indices ν and λ in ϵ are omitted.⁴ We assume that $\mathcal{E}_{\nu\lambda}^{(j)}(0) = E_{\nu\lambda}^j$ for $j = 1, 2, \dots, n$. Then, according to Equations (4) and (40),

$$\tilde{\mathcal{E}}_{\nu\lambda}^{(n)}(r) |_{r=0} = (E_{\nu\lambda} - \alpha_0)^n = \epsilon^n. \quad (41)$$

Therefore, formally, the replacement of H by $\tilde{H}$ and $\mathcal{E}^{(n)}(0)$ by $\tilde{\mathcal{E}}^{(n)}(0)$ is equivalent to setting $\alpha_0 = 0$ in

Equation (5). Consequently, according to Equations (23) and (24), we can formulate

Theorem 2.3: *The n th order energy-dependent constraints are expressed as*

$$\epsilon^j = c_0^{(j)} = \alpha_{-1} c_1^{(j-1)} + A_2 c_2^{(j-1)}, \quad j = 1, 2, \dots, n. \quad (42)$$

In particular,

$$\epsilon = \alpha_{-1} c_1 + A_2 c_2 = -\frac{\alpha_{-1}^2}{A_1} c_0 + A_2 c_2, \quad (43)$$

$$\begin{aligned} \epsilon^2 &= \alpha_{-1} c_1^{(1)} + A_2 c_2^{(1)} \\ &= (\alpha_{-1} \alpha_1 + \alpha_2 A_2) c_0 + \alpha_1 A_2 c_1 + \alpha_{-1}^2 c_2 \\ &\quad + \alpha_{-1} (A_2 + A_3) c_3 + A_2 A_4 c_4, \end{aligned}$$

$$\begin{aligned} \epsilon^3 &= \alpha_{-1} c_1^{(2)} + A_2 c_2^{(2)} = \sum_{i=0}^6 f_i c_i, \\ \dots \quad \dots \quad \dots, \end{aligned} \quad (44)$$

where f_i are linear combinations of products of the potential parameters α_p , $p = -1, 1, 2, 3, 4$ and A_p , $p = 2, 3, 4, 5, 6$. Using relation (43), one can replace the eigenvalue parameter ϵ in the energy-dependent constraints (42) by c_2 .

2.3. The lowest-order constraints

For the reader's convenience, several first coefficients of the expansion of $\psi_{\nu\lambda}^{(0)}$ are given:

$$\begin{aligned} c_0 &= 1, \\ A_1 c_1 &= -\alpha_{-1} c_0, \\ A_2 c_2 &= \epsilon - \alpha_{-1} c_1, \\ A_1 A_3 c_3 &= -\alpha_1 A_1 c_0 - \alpha_{-1}^2 c_1 - \alpha_{-1} (A_1 + A_2) c_2, \\ A_2 A_4 c_4 &= \epsilon^2 - (\alpha_{-1} \alpha_1 + \alpha_2 A_2) c_0 - \alpha_1 A_2 c_1 \\ &\quad - \alpha_{-1}^2 c_2 - \alpha_{-1} (A_2 + A_3) c_3, \\ A_1 A_3 A_5 c_5 &= -[\alpha_{-1}^2 \alpha_1 + \alpha_{-1} \alpha_2 (A_1 + A_2) \\ &\quad + \alpha_3 A_1 A_3] c_0 \\ &\quad - [\alpha_{-1} \alpha_1 (2 A_1 + A_2) + \alpha_2 A_1 A_3] c_1 \\ &\quad - [\alpha_{-1}^3 + \alpha_1 A_1 (A_2 + A_3)] c_2 \\ &\quad - \alpha_{-1}^2 (A_1 + A_2 + A_3) c_3 \\ &\quad - \alpha_{-1} (A_1 A_3 + A_1 A_4 + A_2 A_4) c_4. \end{aligned} \quad (45)$$

3. Example

We consider two Coulomb-interacting particles in a parabolic confinement, i.e. we set $\alpha_{-1} \neq 0$, $\alpha_2 \neq 0$ and $\alpha_i = 0$ if $i \neq -1, 2$. The radial Schrödinger Equation (1) reads

$$\left[-\frac{1}{2\mu} \frac{d^2}{dr^2} + \frac{\lambda(\lambda+1)}{2\mu r^2} + \frac{\alpha_{-1}}{r} + \alpha_2 r^2 \right] \Phi_{\epsilon\lambda}(r) = \epsilon \Phi_{\epsilon\lambda}(r), \quad (46)$$

where subscript ν has been replaced by the corresponding energy ϵ . In the case of two electrons ($\mu = 1/2$, $\alpha_{-1} = 1$) the interaction is repulsive. In the case of two $\mu = 1/2$ particles with opposite charges (electron-positron pair) $\alpha_{-1} = -1$ – the interaction is attractive. The spectrum of the confined system ($\alpha_2 > 0$) in both cases is purely discrete. In the unconfined systems ($\alpha_2 = 0$) the positive energy spectrum is continuous and the continuum spreads from 0 to ∞ . In the case of electron-positron pair discrete states with $\epsilon < 0$ also appear. As it results from Equation (46), the transformation $r \rightarrow -r$ is equivalent to the replacement of α_{-1} by $-\alpha_{-1}$. Under this transformation the wave function changes accordingly, but the eigenvalues remain the same. Note that the last statement is valid only if the same eigenvalue exists in both repulsive and attractive cases. In particular, if $\alpha_2 = 0$ then it is valid for continuous spectra. Otherwise, if $\alpha_2 > 0$, it is valid only for quasi-exact solutions of Equation (46) [17].

According to Equation (45) the coefficients in the asymptotic expansion (7) are equal to

$$\begin{aligned} A_1 c_1 &= -\alpha_{-1}, \\ A_1 A_2 c_2 &= \alpha_{-1}^2 + \epsilon A_1, \\ A_1 A_2 A_3 c_3 &= -\alpha_{-1} [\alpha_{-1}^2 + \epsilon(A_1 + A_2)], \\ A_1 A_2 A_3 A_4 c_4 &= \alpha_{-1}^2 [\alpha_{-1}^2 + \epsilon(A_1 + A_2 + A_3)] \\ &\quad + \epsilon^2 A_1 A_3 - \alpha_2 A_1 A_2 A_3, \\ A_1 A_2 A_3 A_4 A_5 c_5 &= -\alpha_{-1}^3 [\alpha_{-1}^2 + \epsilon(A_1 + A_2 + A_3 + A_4)] \\ &\quad + \alpha_{-1} \epsilon^2 (A_1 A_3 + A_2 A_4 + A_1 A_4) \\ &\quad + \alpha_{-1} \alpha_2 A_2 A_3 (A_1 + A_4), \\ &\dots \dots \dots \end{aligned} \quad (47)$$

It is convenient to split expansion (7) to two parts: the first one ($F_{\alpha_{-1}}$) one describing the interaction of unconfined particles and the second one (Δ_{α_2}), describing the effect of confinement:

$$\psi_{\epsilon\lambda}(r) = F_{\alpha_{-1}}(r) + \Delta_{\alpha_2}(r), \quad (48)$$

where in F and Δ subscripts ϵ and λ have been omitted. Using Equations (21) and (45) for $s = 7$, $\alpha_{-1} = 1$, and

$\lambda = 0$, i.e. for two electrons in a 1S state, we get

$$\begin{aligned} F_1(r) &= 1 + \frac{r}{2} + \left(\frac{1}{2} - \epsilon\right) \frac{r^2}{6} + \left(\frac{1}{8} - \epsilon\right) \frac{r^3}{18} \\ &\quad + \left[\left(\frac{1}{20} - \epsilon\right) \frac{1}{144} + \frac{\epsilon^2}{120}\right] r^4 \\ &\quad + \left[\left(\frac{1}{40} - \epsilon\right) \frac{1}{2160} + \frac{23\epsilon^2}{10800}\right] r^5 \\ &\quad + \left[\left(\frac{1}{70} - \epsilon\right) \frac{1}{51840} + \frac{\epsilon^2}{720} \left(\frac{7}{45} - \frac{\epsilon}{7}\right)\right] r^6 \\ &\quad + \left[\left(\frac{1}{112} - \epsilon\right) \frac{1}{1814400} + \frac{11\epsilon^2}{37800} \left(\frac{1}{24} - \frac{\epsilon}{7}\right)\right] r^7 \\ &\quad + O(r^8), \end{aligned} \quad (49)$$

and

$$\begin{aligned} \Delta_{\alpha_2}(r) &= \frac{\alpha_2}{20} \left(r^4 + \frac{11}{30} r^5 + \frac{61 - 130\epsilon}{1260} r^6 \right. \\ &\quad \left. + \frac{59 - 498\epsilon}{17640} r^7 \right) + O(r^8). \end{aligned} \quad (50)$$

The expression for $\alpha_{-1} = -1$ can be obtained by the substitution $r \rightarrow -r$. The parabolic confinement does not affect c_1 , c_2 and c_3 . Therefore, up to the cubic term, the asymptotic expansion (7) of $\psi_{\epsilon\lambda}$ is the same whether or not there is a parabolic confinement.

In Figure 1 the wave functions of the first three 1S states of harmonium ($\epsilon = 2230, 4134, 6074$ mH) and of the confined positronium ($\epsilon = 612, 2805, 4892$ mH) with $\alpha_2 = 1/4$, for $r < 1.5$ bohr, represented by solid lines, are compared with the results given by expansion (48) including only the free-particle term F_1 (dashed lines) and also the confinement contribution Δ_{α_2} (dash-dotted lines). Surprisingly, the free-particle wave functions corresponding to the continuous spectra are nearly the same as the wave functions of the bound states of the confined systems, also for relatively large r .⁵ A contribution due to the confinement appears starting at c_4 , but for both c_4 and c_5 , it is an energy-independent constant term.

The convergence pattern of expansion (48) is shown in Figure 2, where differences between the exact ground state wave function of harmonium and the expansion (48) with the number of terms varying from 2 to 8 are plotted versus r . Line 1 corresponds to the two-term expansion, i.e. to Kato's cusp condition. Line 7 corresponds to the 8-term expansion including powers of r from 0 to 7. The dashed lines refer to the unconfined pair of electrons (with term Δ_{α_2} neglected).

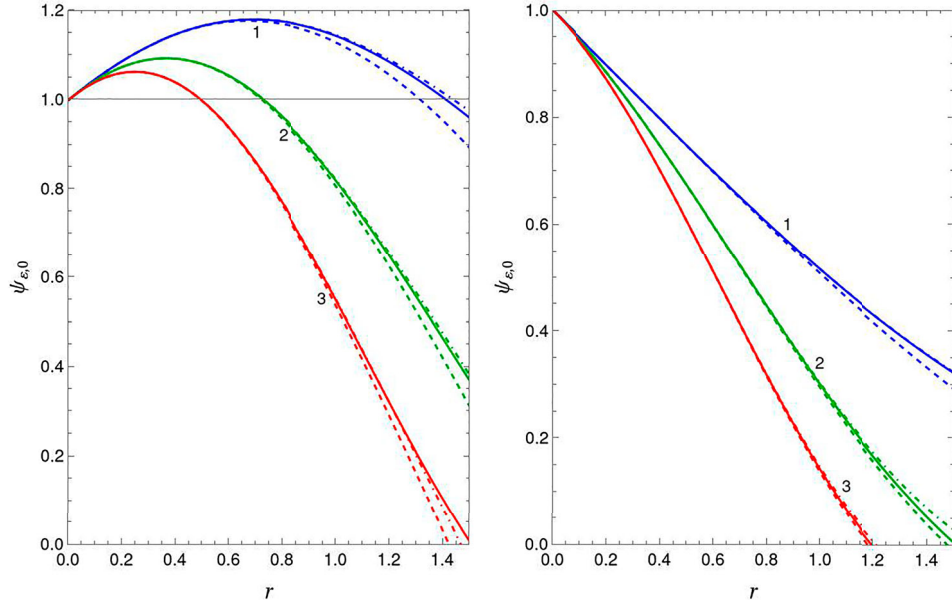


Figure 1. Solid lines: the exact wave functions $\psi_{\epsilon,0}(r)$ of the first three $1S$ states of harmonium (left panel) and of the confined positronium (right panel), versus r . Dashed lines – first eight expansion terms representing continuous spectrum wave functions of the unconfined systems [Equation (49)]; dash-dotted lines – the same, but including also the effect of confinement [Equation (50)]. The confinement parameter $\alpha_2 = 1/4$; labels 1, 2, 3, refer to the consecutive states.

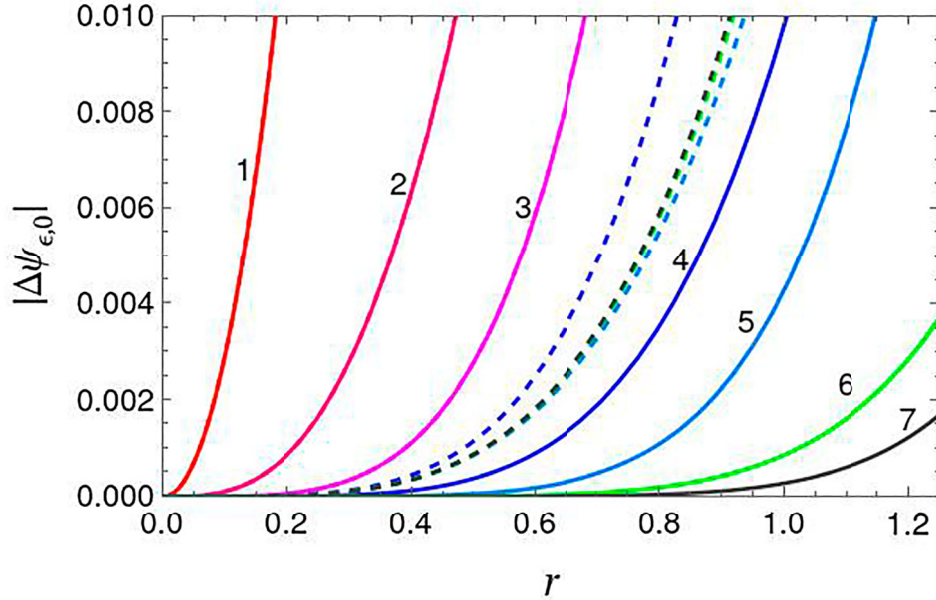


Figure 2. Differences between the exact ground state wave function of harmonium and the expansion given by Equation (48) for $\alpha_2 = 1/4$. Labels 1, 2, $\dots$, 7 are equal to s , the highest power of r included in the expansion. Results for the unconfined pair of electrons for $s = 1, 2, 3$ are the same as for the confined pair. The effect of ignoring confinement is indicated by dashed lines which correspond to $s = 4, 5, 6, 7$ and $\Delta\alpha_2 = 0$.

4. Final remarks

We introduced the notion of the local energy of the n th order (3) and derived conditions which prevent the local energy of an arbitrary order to diverge at the coalescence point, referred to as the *energy-independent coalescence constraints*. The wave function neither has to describe a

bound state nor be a Hamiltonian eigenfunction. Only its asymptotic expansion at $r = 0$ has to exist. By using the energy-independent coalescence constraints we can express the wave function in the vicinity of $r = 0$ as a linear combination of even powers of r with each term of this combination modified by a polynomial composed of

the odd powers with coefficients fixed by the coalescence constraints [Equations (32) and (33)].

From the requirement that the n th order local energy at $r = 0$ is proportional to the n th power of the eigenvalue, we derived the *energy-dependent constraints* fulfilled by the *even* coefficients of the expansion of the wave function. The coefficients c_{2i} , $i = 1, 2, \dots$, can be expressed as the i th order polynomials of the eigenvalue or, alternatively, of c_2 . The complete set of the coalescence constraints is equivalent to the *general coalescence conditions* of Kurokawa *et al.* [10–12].

In the coalescence region the Coulomb wave functions corresponding to the discrete spectrum of particles confined in a parabolic potential are nearly the same as the wave functions of the unconfined particles with the same energies, but belonging to the continuous part of the spectrum. This effect depends on the strength of confinement. The wave function of harmonium behaves as the wave function of two electrons for small r and as the wave function of the harmonic oscillator for large r . The range of r where the harmonic oscillator behaviour dominates extends with increasing α_2 . For a moderate confinement (as e.g. $\alpha_2 = 1/4$), differences between the wave functions with confinement effects included and neglected only become noticeable for $r > 1$.

Notes

1. It is convenient to use the radial Hamiltonian in the self-conjugate form which does not contain the first-order derivative.
2. Equation (3) is meaningful if $H^n \Psi(r)$ exists, i.e. if Ψ is $(2n)$ -fold differentiable in its domain. As shown by Fournais *et al.* [15], if the other electron coordinates do not coincide, then in a neighbourhood of the coalescence point Coulombic wave functions are analytic, i.e. they are differentiable an arbitrary number of times.
3. See also an early study on the coalescence conditions for non-Coulombic potentials by Silanes *et al.* [14].
4. Note that a shift in the energy scale does not affect the eigenfunctions.
5. Explicit expressions for the continuous spectrum wave functions can be found, e.g. in the monograph by Bethe and Salpeter [18]. The expansion given by Equation (48) with $\Delta_{\alpha_2}(r) = 0$ is the same as the one obtained from the expansion of the exact eigenfunctions.

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No potential conflict of interest was reported by the author(s).

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Appendix. Graphical representations

The derivation of energy-independent coalescence conditions is facilitated by a graphical representation of Equations (21) and (26). The graphs are composed of *vertices* distributed in rows and linked by *arcs*. A vertex corresponds to a specific coefficient $c_i^{(j)}$, shown in the vertex. To each arc we assign an *arc index*. Sub-graphs composed of vertex $c_i^{(n)}$ and vertices

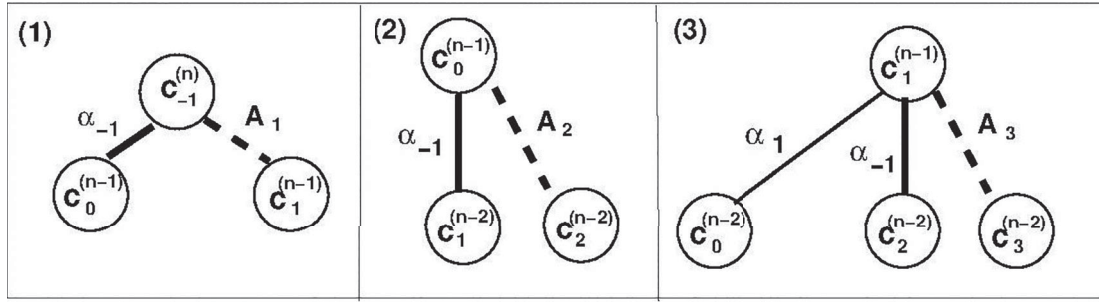


Figure A1. Graphical representations of Equations (A1) – panel (1), (A2) – panel (2), and (A3) – panel (3). Arcs corresponding to α_0 are not shown since they do not contribute to the constraints.

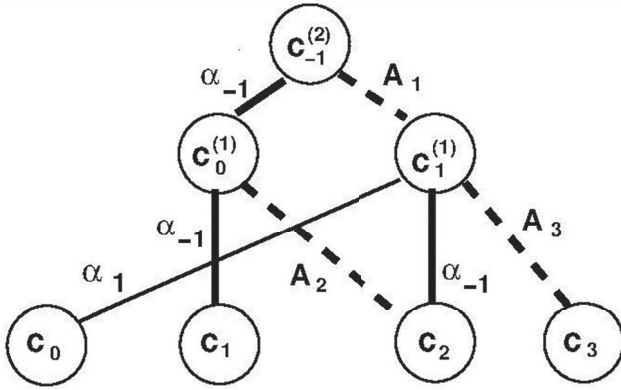


Figure A2. Graphical representation of Equation (A4).

$c_j^{(n-1)}$ together with arcs linking these vertices are referred to as *segments*. Segments representing equations

$$c_{-1}^{(n)} = \alpha_{-1} c_0^{(n-1)} + A_1 c_1^{(n-1)}, \quad (\text{A1})$$

$$c_0^{(n-1)} = \alpha_{-1} c_1^{(n-2)} + A_2 c_2^{(n-2)}, \quad (\text{A2})$$

$$c_1^{(n-1)} = \alpha_1 c_0^{(n-2)} + \alpha_{-1} c_2^{(n-2)} + A_3 c_3^{(n-2)}, \quad (\text{A3})$$

i.e. Equation (21) for $i = -1, 0, 1$, are shown, respectively, in panels (1), (2), (3) of Figure A1. Equation

$$c_{-1}^{(2)} = \alpha_{-1} c_0^{(1)} + A_1 c_1^{(1)} = \alpha_1 A_1 c_0 + \alpha_{-1}^2 c_1 + \alpha_{-1} (A_1 + A_2) c_2 + A_1 A_3 c_3. \quad (\text{A4})$$

is represented in Figure A2 – the graph has been obtained by connecting three segments of Figure A1 (for $n = 2$) into one diagram.

In general, expression (26) for $c_{-1}^{(n)}$ is equal to the sum of products of the arc indices and the coefficients $c_i^{(n)}$, taken over all paths leading from $c_{-1}^{(n)}$ to all vertices of the selected level in the graph (in one level there are vertices corresponding to a given order of the local energy). Vertices of adjacent levels are linked by arcs – if $c_a^{(j)} = \dots + h c_b^{(j-1)} + \dots$, then vertices $c_a^{(j)}$ and $c_b^{(j-1)}$ are linked by an arc and the arc index is equal h . By the construction, only paths going down from the uppermost vertex are allowed.

The uppermost part (the first five rows) of the most general graph (all $\alpha_p \neq 0$) is shown in Figure A3. Contributions from α_{-1} and from A_j are present in all orders. Contributions from α_1 start from the second order. From the third order up, we have also contributions from α_2 and α_3 . In the next order contributions from α_4 and α_5 appear. And so on – each next order activates two more terms of the expansion of $V(r)$.

The graph corresponding to the pure Coulomb potential, i.e. to the case of $\alpha_p = 0$ if $p \neq -1$, is given in Figure A4. It is isomorphic with the Pascal triangle. There are $\binom{j}{p}$ paths one can reach node $c_{j+p-1}^{(n-j)}$ starting from node $c_{-1}^{(n)}$. With each path we associate a product of all arc indices A_i taken along this path. The coefficient $\mathcal{A}_p^{(j)}$ introduced in Equation (36) is equal to the sum of these products extended over all $\binom{j}{p}$ paths. For example, nodes $c_{-1}^{(n)}$ and $c_6^{(n-4)}$ are linked by $\binom{4}{3} = 4$ paths and $\mathcal{A}_p^{(j)} = A_1 A_3 A_5 + A_1 A_3 A_6 + A_1 A_4 A_6 + A_2 A_4 A_6$.

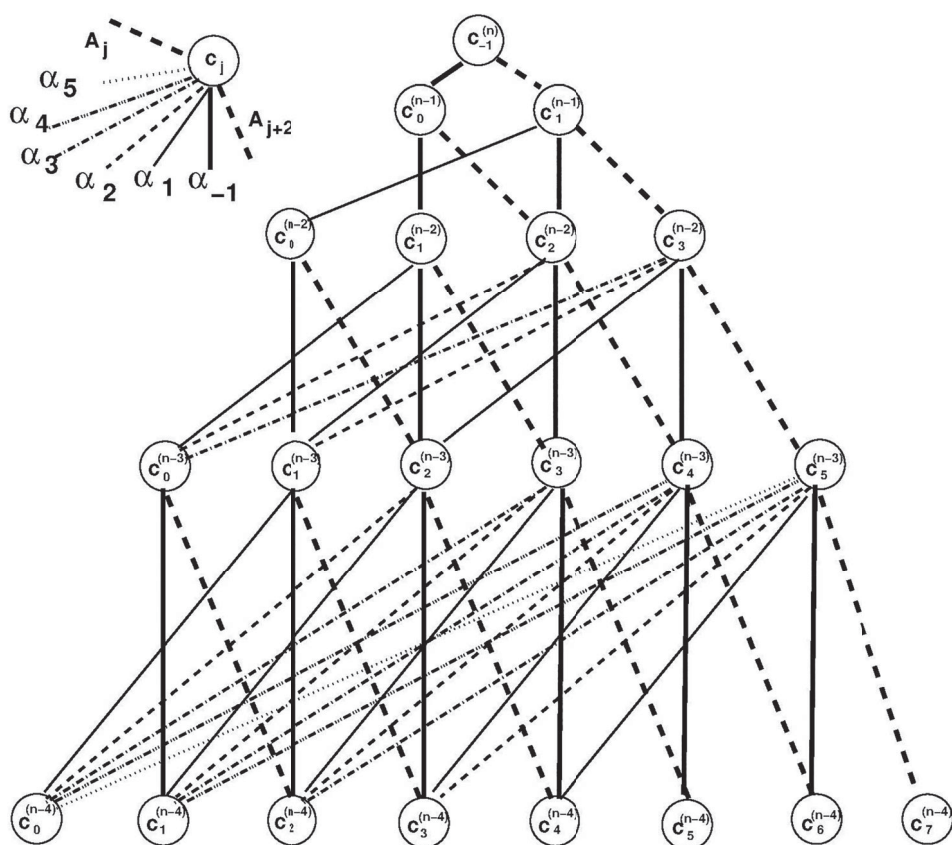


Figure A3. The first five rows of graphical representation of Equation (26). Arcs corresponding to α_0 are not shown since they do not contribute to the constraints (see Theorem 2.1).

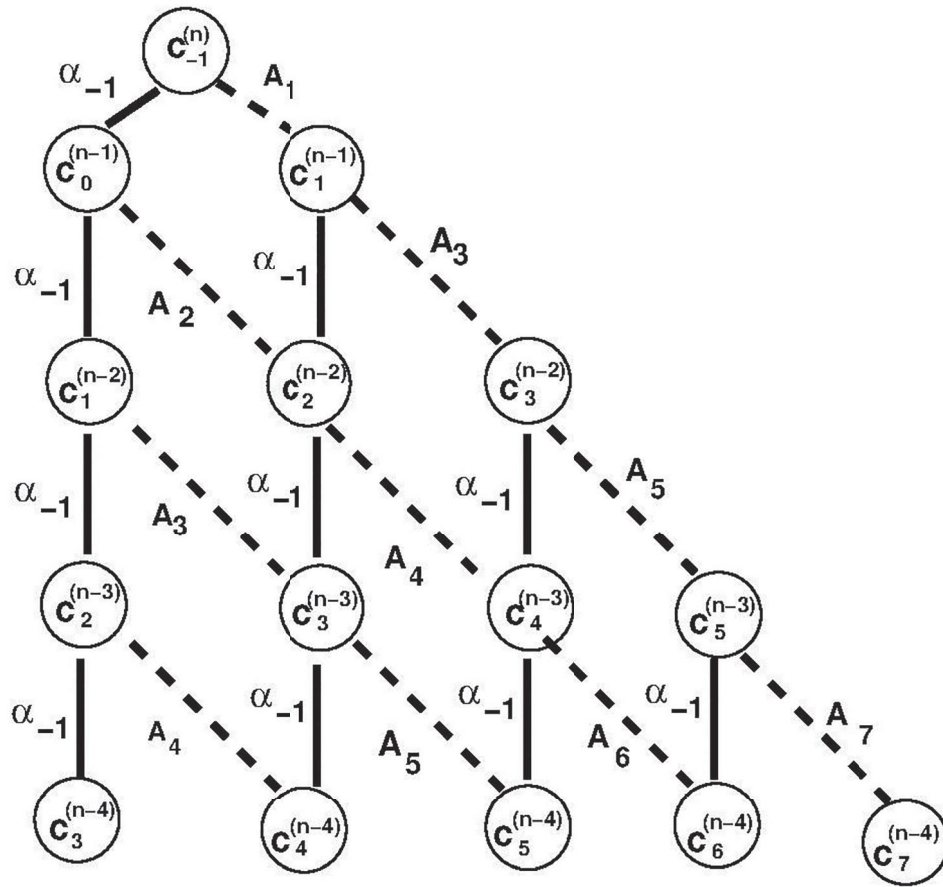


Figure A4. Graph for the case of the pure Coulomb potential ($\alpha_p = 0$ if $p \neq -1$).