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Scattering and bound-state problems with non-local potentials: application of the variable-phase approach

O Kidun[1], **N Fominykh**[1] **and J Berakdar**[2,3]

[1] Max-Planck Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany
[2] ITAMP at the Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA

E-mail: okidun@mpi-halle.de

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Abstract

Following the framework of the variable-phase approach, we derive an equation for determining the scattering amplitude of a non-relativistic quantum particle in a non-local potential. Its solution implies the integration of the Volterra integro-differential equation of the first kind and allows determination of bound-state energies and wavefunctions. A fast numerical scheme for the solution of these equations is suggested and it is demonstrated that the proposed method requires the numerical efforts of the same order as in the local potential case.

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1. Introduction

In the early 1960s, an elegant approach was developed independently by Calogero [1] and Babikov [2] in which the treatment of the quantum mechanics of a non-relativistic particle was formulated in terms of observables, such as the scattering phase shifts and the scattering amplitudes. Accordingly, this general scheme is referred to as the variable-phase approach (VPA), or the phase-amplitude method. Technically, the VPA makes use of the fact that any second-order differential equation (DE), and in particular the Schrödinger equation, is equivalent to a pair of first-order coupled DEs. These DEs determine the so-called phase and amplitude functions. A favourable feature of the VPA is that a decoupling of the two first-order DEs can be achieved [1, 2]. This is advantageous in so far as in many cases the solution of only one of the two DEs is required to obtain the desired physical quantities, e.g. for the evaluation of the scattering cross section it suffices to know only the scattering phase shifts. If the second first-order DE is solved one can completely restore the energy spectrum

[3] On leave from the Max-Planck Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany.

and the wavefunctions and achieve thus the information equivalent to the traditional solution of the Schrödinger equation. In this way, it is possible to treat both scattering and bound-state problems. Due to its generality, the VPA has been applied in various fields [5–9]: for example, the scattering of positrons from rare atomic gases has been treated by means of the VPA [5]; doubly excited states of He have been described by VPA [6]; and the quasi-particle lifetimes in a charged Bose gas and in cuprates have been determined using the VPA [7]. Furthermore, for the calculations of the degree of ionization of a non-degenerate two-dimensional electron–hole plasma, the VPA has been used [8] to account simultaneously for all bound and unbound states in a screened Coulomb potential. Recently, we utilized the VPA for the description of the scattering and the bound states of metal clusters and fullerenes [9].

In this paper, we derive an equation for the scattering amplitude (SA) of a particle subjected to a non-local potential (equation (20)). Furthermore, we propose an efficient numerical method to extract simultaneously the bound and scattering states. The case of non-local potentials is encountered in various situations; for example, in a mean-field treatment of many-electron systems the exchange interaction results in a non-local potential term that needs to be treated accurately. The local version of the equation for the SA (see equation (14) in this paper) and the non-local version of the equation for the scattering phase (equation (6)) have been already published [3, 4].

The plan of this paper is as follows. In section 2 we recall the basic steps of the VPA and we derive the phase equation for the non-local potential. In section 3 we obtain the first result of our paper, the equation for the SA for the non-local potential. Traditional treatments of the eigenvalue problem for the non-local potential imply the expansion over a set of basis functions. In contrast, in the present method we solve for the first-order Volterra integro-differential equations, and hence the solution is independent of the choice of the basis. In section 4 we propose a fast finite-difference scheme for the numerical solution of these DEs and we demonstrate that the present technique requires numerical efforts, which are of the same order as those for the local potential case.

2. Phase-amplitude equations in the non-local potential

The motion of a non-relativistic, spinless particle with the energy k^2 in the presence of the Hermitian, non-local potential $V(\mathbf{r}, \mathbf{r}') = V(\mathbf{r}', \mathbf{r})$ is governed by the Schrödinger wave equation (throughout we use units in which $2m = 1 = \hbar$, $Z = 1$, where m and Z are the mass and the charge of the particle)

$$\triangle \Psi(\mathbf{r}) + k^2 \Psi(\mathbf{r}) = \int \mathrm{d}\mathbf{r}'\, V(\mathbf{r}, \mathbf{r}') \Psi(\mathbf{r}'). \tag{1}$$

In the absence of a preferential direction in space, the potential $V(\mathbf{r}, \mathbf{r}')$ is a function of only the scalar variables r^2, r'^2, $(\mathbf{r}, \mathbf{r}') = rr' \cos\theta$. Therefore it is advantageous to operate in spherical coordinates in which case equation (1) admits separation of angular and radial motion. The radial part $u_\ell(r)$ of the wavefunction is determined by the equation

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2} u_\ell(r) + \left(k^2 - \frac{\ell(\ell+1)}{r^2} \right) u_\ell(r) = \int_0^\infty \mathrm{d}r'\, V_\ell(r, r') u_\ell(r') \tag{2}$$

where $V_\ell(r, r') = V_\ell(r', r) = 2\pi rr' \int_{-1}^{1} V_\ell(r, r') P_\ell(\cos\theta)\, \mathrm{d}(\cos\theta)$, ℓ is the orbital quantum number. The idea of the VPA is not to solve directly for u_ℓ but to express it in terms of physical quantities, to solve for these quantities and, if desired, to construct $u_\ell(r)$. For this purpose, we introduce the functions $\alpha_\ell(r)$ and $\delta_\ell(r)$ such that

$$u_\ell(r) = \alpha_\ell(r)[\cos\delta_\ell(r)\, j_\ell(kr) - \sin\delta_\ell(r) n_\ell(kr)] \equiv \alpha_\ell(r) F_\ell(r) \tag{3}$$

and we impose the additional condition on the derivative

$$\frac{\mathrm{d}}{\mathrm{d}r}u_\ell(r) = \alpha_\ell(r)\left[\cos\delta_\ell(r)\frac{\mathrm{d}}{\mathrm{d}r}j_\ell(kr) - \sin\delta_\ell(r)\frac{\mathrm{d}}{\mathrm{d}r}n_\ell(kr)\right]. \tag{4}$$

Here $j_\ell(kr)$ and $n_\ell(kr)$ are Riccati–Bessel functions defined as regular and irregular solutions of the Schrödinger equation for a free particle. The second condition defined by equation (4) is necessary since we introduce two new functions instead of one. This constraint is equivalent to

$$\frac{\mathrm{d}\alpha_\ell(r)}{\mathrm{d}r}F_\ell(r) = \alpha_\ell(r)\frac{\mathrm{d}\delta_\ell(r)}{\mathrm{d}r}G_\ell(r) \tag{5}$$

where $G_\ell(r) = \sin\delta_\ell(r)\,j_\ell(kr) + \cos\delta_\ell(r)n_\ell(kr)$.

The functions $\delta_\ell(r)$ and $\alpha_\ell(r)$ are conventionally referred to as the phase and the wave-amplitude functions, respectively. At each radial position R the values of the functions $\delta_\ell(R)$ and $\alpha_\ell(R)$ have a precise physical meaning; they coincide correspondingly with the partial scattering phase $\widehat{\delta}_\ell^{(R)}$ and with the asymptotic amplitude $\widehat{\alpha}_\ell^{(R)}$ of the wavefunction of the particle subjected to the potential $V_\ell^{(R)}$ (where a hat denotes an observable). The potential $V_\ell^{(R)}$ is obtained from a cut-off of the potential $V_\ell(r, r')$ at the position R, i.e. $V_\ell^{(R)}(r, r') = V_\ell(r, r')\theta(R - r)\theta(R - r')$, where θ is the step function $\theta(x > 0) = 1, \theta(x < 0) = 0$. This property allows a detailed investigation of the accumulation of the phase shift and the asymptotic wave amplitude due to the structure of the potential. Correspondingly, the asymptotic value of $\delta_\ell(r)$ at $r \longrightarrow \infty$ gives the scattering phase for the genuine potential $V_\ell(r, r')$: $\delta_\ell(\infty) = \widehat{\delta}_\ell$.

Substitution of equations (3) and (5) into (2) leads to (the derivation is given in the appendix)

$$\frac{\mathrm{d}\delta_\ell(r)}{\mathrm{d}r} = -\frac{F_\ell(r)}{k}\int_0^\infty \mathrm{d}r'\,V_\ell(r, r')F_\ell(r')\exp\left[-\int_{r'}^{r}\frac{G_\ell(s)}{F_\ell(s)}\cdot\dot{\delta}_\ell(s)\,\mathrm{d}s\right]. \tag{6}$$

Here and below $\dot{y}(x)$ denotes $\frac{\mathrm{d}y(x)}{\mathrm{d}x}$. The initial condition for the equation (6) is $\delta_\ell(0) = 0$ which corresponds to the absence of the irregular solution at the origin (or the absence of the phase shift $\delta_\ell(0) = \widehat{\delta}_\ell^{(R=0)} = 0$ for the zero potential $V_\ell^{(R=0)}(r, r') = 0\,\forall r, r'$).

Note that the equation for the phase function does not contain the wave-amplitude function $\alpha_\ell(r)$. This has a profound physical meaning and stems from the fact that the normalization of the wavefunction is inessential for the scattering problems. The equation for the derivative of $\alpha_\ell(r)$, equation (5), can be explicitly integrated after $\delta_\ell(r)$ has been determined, i.e.

$$\alpha(r) = \alpha(0)\exp\left(\int_0^r\frac{G_\ell(s)}{F_\ell(s)}\cdot\dot{\delta}_\ell(s)\,\mathrm{d}s\right) \tag{7}$$

where $\alpha_\ell(0)$ plays the role of a normalization constant.

Another useful equation for determining the phase function is

$$\frac{\mathrm{d}\delta_\ell(r)}{\mathrm{d}r} = \left(-\frac{1}{k}\right)F_\ell^2(r)\int_0^\infty \mathrm{d}r'\,V_\ell(r, r')\exp\left[-\int_{r'}^{r}\frac{N_\ell(s)}{F_\ell(s)}\,\mathrm{d}s\right] \tag{8}$$

with

$$N\alpha_\ell(s) = \cos\delta_\ell(s)\frac{\mathrm{d}j_\ell(ks)}{\mathrm{d}s} - \sin\delta_\ell(r)\frac{\mathrm{d}n_\ell(kr)}{\mathrm{d}s}.$$

This relation is readily verified by the following identity that will be utilized below

$$\mathrm{d}F = N\mathrm{d}s - G\mathrm{d}\delta \quad \Rightarrow \quad \int_{r'}^{r}\left(-\frac{G}{F}\,\mathrm{d}\delta\right) = \int_{r'}^{r}\left(\frac{\mathrm{d}F}{F} - \frac{N\,\mathrm{d}s}{F}\right)$$
$$= \ln\left(\frac{F(r)}{F(r')}\right) - \int_{r'}^{r}\frac{N(s)}{F(s)}\,\mathrm{d}s. \tag{9}$$

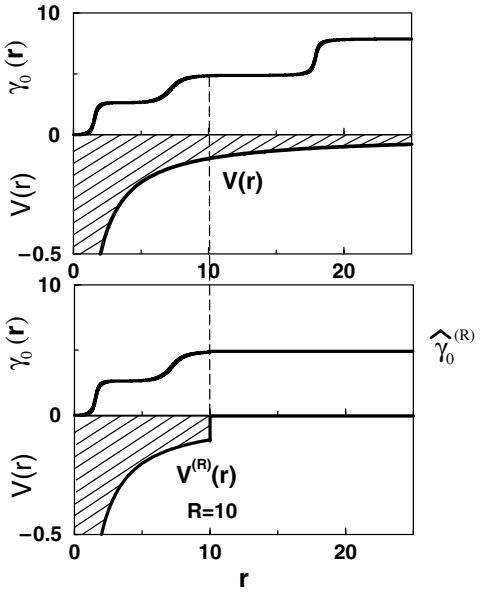

Figure 1. The behaviour of the arctangent of the SA function $\gamma_0(r)$ built for the Coulomb potential $V(r) = -1/r$ (upper plot) and for the Coulomb cut-off at $R = 10$ (lower plot). At the radial distance R, the value of $\gamma_0(r = R)$ coincides with the arctangent of the SA $\widehat{\gamma}_0^{(R)} = \arctan(\kappa \widehat{\mathcal{F}}_0^{(R)})$, associated with the cut-off potential $V^{(R)}(r)$.

3. Transition to the SA representation

The partial SA $\widehat{\mathcal{F}}_\ell$ is obtained from the partial scattering phase via the well-known relation [10] $\widehat{\mathcal{F}}_\ell = \frac{1}{k} \sin\widehat{\delta}_\ell \, \mathrm{e}^{\mathrm{i}\widehat{\delta}_\ell}$. Accordingly, the SA function is introduced as

$$\mathcal{F}_\ell(r) \equiv \frac{1}{k} \sin\delta_\ell(r) \, \mathrm{e}^{\mathrm{i}\delta_\ell(r)}. \tag{10}$$

Analogously to the previous section, the value of the SA function $\mathcal{F}_\ell(r = R)$ is equal to the SA $\widehat{\mathcal{F}}_\ell^{(R)}$ associated with the cut-off potential $V_\ell^{(R)}$ (see figure 1 for details). In the following, we derive an integro-differential equation for the SA function and then we regularize it to make it suitable for the determination of bound-state energies of a particle in a non-local potential. To this end we introduce the auxiliary functions

$$\begin{aligned} f_\ell(r) &\equiv k\mathcal{F}_\ell(r) = \mathrm{e}^{\mathrm{i}\delta_\ell(r)} \sin\delta_\ell(r) \\ \widetilde{F}_\ell(r) &\equiv F_\ell(r) \, \mathrm{e}^{\mathrm{i}\delta_\ell(r)} = j_\ell(r) + \mathrm{i}h_\ell^{(1)}(kr) f_\ell(r) \\ \widetilde{G}_\ell(r) &\equiv G_\ell(r) \, \mathrm{e}^{\mathrm{i}\delta_\ell(r)} = n_\ell(r) + h_\ell^{(1)}(r) f_\ell(r). \end{aligned} \tag{11}$$

Now we express $\delta_\ell(r)$ through $f_\ell(r)$ and we make use of the relation between their derivatives

$$\frac{\mathrm{d}\delta_\ell(r)}{\mathrm{d}r} = \frac{1}{2\mathrm{i}f_\ell(r) + 1} \frac{\mathrm{d}f_\ell(r)}{\mathrm{d}r}. \tag{12}$$

Employing the definitions (3) and (5), we can transform the phase equation (6) to an equation for the function $f_\ell(r)$

$$\begin{aligned} \frac{\mathrm{d}f_\ell(r)}{\mathrm{d}r} = &\left(-\frac{1}{k}\right) \sqrt{2\mathrm{i}f_\ell(r) + 1} \, \widetilde{F}_\ell(r) \\ &\times \int_0^\infty \mathrm{d}r' \, V_\ell(r, r') \frac{\widetilde{F}_\ell(r')}{\sqrt{2\mathrm{i}f_\ell(r') + 1}} \exp\left[-\int_{r'}^{r} \frac{\dot{f}_\ell(s) \, \mathrm{d}s}{(2\mathrm{i}f_\ell(s) + 1)} \frac{\widetilde{G}_\ell(s)}{\widetilde{F}_\ell(s)}\right] \end{aligned} \tag{13}$$

subject to the initial condition $f_\ell(0) = 0$. It is readily verified that equation (13) reduces to the known equation for the local potential case, when $V(r, r') = V(r')\delta(r - r')$ (cf [3, 4]):

$$\frac{\mathrm{d}f_\ell(r)}{\mathrm{d}r} = -\frac{1}{k} \cdot V_\ell(r)\widetilde{F}_\ell^2(r). \tag{14}$$

In the complex plane of the wave vector k, each partial SA describes stationary and quasi-stationary states characterized by a certain orbital momentum ℓ. If the partial SA has a pole on the positive imaginary semi-axis ($k = \mathrm{i}\kappa_n, \kappa_n \in \mathcal{R}^+$), then this value of k corresponds to the energy of a stationary state in the discrete spectrum: $E_n = (\mathrm{i}\kappa_n)^2 < 0$. The condition, from which the bound-state energy can be determined, reads:

$$f_\ell(\infty; \kappa_n) = \infty. \tag{15}$$

Now we rewrite equation (13) for $k = \mathrm{i}\kappa, \kappa > 0$. The Riccati–Bessel functions of the imaginary argument can be expressed through the modified Riccati–Bessel functions of the real argument $p_\ell(\kappa r)$ and $q_\ell(\kappa r)$

$$j_\ell(\mathrm{i}\kappa r) = \beta p_\ell(\kappa r) \tag{16}$$

$$n_\ell(\mathrm{i}\kappa r) = \frac{\mathrm{i}}{\beta}[\beta^2 p_\ell(\kappa r) - q_\ell(\kappa r)] \tag{17}$$

$$h_\ell^{(1)}(\mathrm{i}\kappa r) = \frac{1}{\beta} q_\ell(\kappa r) \tag{18}$$

with $\beta = (\mathrm{i})^{\ell+1}$. The integrand occurring in equation (13) can then be written as

$$\begin{aligned}
&\exp\left[-\int_{r'}^{r} \frac{\mathrm{d}f_\ell(s)}{2\mathrm{i}f_\ell(s)+1} \frac{\hat{G}_\ell(s)}{\hat{F}_\ell(s)}\right] \\
&\quad = \exp\left[-\int_{r'}^{r} \frac{\mathrm{d}f_\ell(s)}{2\mathrm{i}f_\ell(s)+1} \frac{\mathrm{i}\left[\beta^2 p_\ell(\kappa s) - q_\ell(\kappa s)\,(\mathrm{i}f_\ell(s)+1)\right]}{\left[\beta^2 p_\ell(\kappa s) + q_\ell(\kappa s)\,(\mathrm{i}f_\ell(s))\right]}\right] \\
&\quad = \exp\left[-\int_{r'}^{r} \frac{1}{2}\frac{\mathrm{d}(2\mathrm{i}f_\ell(s)+1)}{2\mathrm{i}f_\ell(s)+1} - \frac{q_\ell(\kappa s)\,\mathrm{d}(\mathrm{i}f_\ell(s))}{q_\ell(\kappa s)\mathrm{i}f_\ell(s) + \beta^2 p_\ell(\kappa s)}\right].
\end{aligned} \tag{19}$$

The integration of the first term yields

$$\exp\left\{-\frac{1}{2}\ln\left[\frac{2\mathrm{i}f_\ell(r)+1}{2\mathrm{i}f_\ell(r')+1}\right]\right\} = \frac{\sqrt{2\mathrm{i}f_\ell(r')+1}}{\sqrt{2\mathrm{i}f_\ell(r)+1}}.$$

This cancels the analogous square roots in equation (13).

Using the identity (9) we obtain the first-kind Volterra integro-differential equation that determines the function $\mathrm{i}f_\ell(r)$

$$\begin{aligned}
\frac{\mathrm{d}(\mathrm{i}f_\ell(r))}{\mathrm{d}r} &= -\frac{2}{\beta^2\kappa}\left[\mathrm{i}f_\ell(r)q_\ell(\kappa r) + \beta^2 p_\ell(\kappa r)\right]^2 \\
&\quad \times \int_0^r \mathrm{d}r'_\ell\, V(r, r') \cosh\left\{-\int_{r'}^{r} \mathrm{d}s \frac{\mathrm{i}f_\ell(s)\dot{q}_\ell(\kappa s) + \beta^2 \dot{p}_\ell(\kappa s)}{\mathrm{i}f_\ell(s)q_\ell(\kappa s) + \beta^2 p_\ell(\kappa s)}\right\}.
\end{aligned} \tag{20}$$

The pre-factor 2, the finite upper limit of the external integral on the right-hand side of equation (20) and the cosh function are due to a symmetrization of the integrand with respect to an interchange of r and r'. It is convenient to make the substitution $\mathrm{i}f_\ell(r) \equiv \beta^2 y_\ell(r)$ in which case equation (20) is transformed into an equation for the *real* function $y_\ell(r)$, i.e.

$$\begin{aligned}
\frac{\mathrm{d}y_\ell(r)}{\mathrm{d}r} &= -\frac{2}{\kappa}\left[y_\ell(r)q_\ell(\kappa r) + p_\ell(\kappa r)\right]^2 \\
&\quad \times \int_0^r \mathrm{d}r'\, V_\ell(r, r') \cosh\left\{-\int_{r'}^{r} \mathrm{d}s \frac{y_\ell(s)\dot{q}_\ell(\kappa s) + \dot{p}_\ell(\kappa s)}{y_\ell(s)q_\ell(\kappa s) + p_\ell(\kappa s)}\right\}.
\end{aligned} \tag{21}$$

Since we have assumed $V_\ell(r, r')$ to be Hermitian and since the functions $p_\ell(\kappa r)$ and $q_\ell(\kappa r)$ are real, the initial condition $y_\ell(0, \kappa) = 0$ implies that $y_\ell(r, \kappa)$ is real everywhere. The bound state exists at the eigenvalue $E = -\kappa^2$ when $y_\ell(\infty, \kappa)$ has a pole.

3.1. Regularization

The regularization of equation (21) can be made in two different ways: (a) by the inverse function $y = 1/\phi$; or (b) by the tangent function $y = \tan\gamma$. In the first case, we obtain the following differential equation for ϕ_ℓ

$$\frac{\mathrm{d}\phi_\ell(r)}{\mathrm{d}r} = \frac{2}{\kappa}\left[q_\ell(\kappa r) + \phi_\ell(r)\, p_\ell(\kappa r)\right]^2 \times \int_0^r \mathrm{d}r'\, V_\ell(r, r') \cosh\left\{-\int_{r'}^r \mathrm{d}s \frac{\dot{q}_\ell(\kappa s) + \phi_\ell(s)\,\dot{p}_\ell(\kappa s)}{q_\ell(\kappa s) + \phi_\ell(s)\, p_\ell(\kappa s)}\right\}. \tag{22}$$

Then the eigenvalue problem is reduced to finding the zeros of $\phi_\ell(\infty, \kappa)$.

The second way (b) yields the following equation for γ_ℓ with the initial condition $\gamma_\ell(0, \kappa) = 0$

$$\frac{\mathrm{d}\gamma_\ell(r)}{\mathrm{d}r} = -\frac{2}{\kappa}\left[q_\ell(\kappa r)\sin\gamma_\ell(r) + p(\kappa r)\cos\gamma_\ell(r)\right]^2 \times \int_0^r \mathrm{d}r'\, V_\ell(r, r') \times \cosh\left\{-\int_{r'}^r \mathrm{d}s \frac{\sin\gamma_\ell(s)\dot{q}_\ell(\kappa s) + \cos\gamma_\ell(s)\,\dot{p}_\ell(\kappa s)}{\sin\gamma(s) q_\ell(\kappa s) + \cos\gamma_\ell(s)\, p_\ell(\kappa s)}\right\}. \tag{23}$$

The condition for the occurrence of bound states is $\gamma_\ell(\infty, \kappa) = (2n - 1)\pi/2, n \in \mathcal{N}$. It is useful to note that the sign of the derivatives of the functions $\delta_\ell(r)$, $y_\ell(r)$, $\phi_\ell(r)$, $\gamma_\ell(r)$ is fully specified by the sign of the potential $V_\ell(r, r')$, as can be inferred from the equations (8) and (21)–(23).

4. Finite-difference scheme

The main difference between the numerical treatments of the local and the non-local potentials is that, instead of an ordinary differential equation (cf equation (14)) in the first case, one has to deal with the integro-differential equation (cf equations (22) or (23)). For concreteness, let us consider equation (23). While for local potentials rather fast, well-known methods (e.g. the Runge–Kutta method) can be applied, for non-local potentials one has to perform two additional integrations at each step of the calculations of the derivatives. Evidently, the numerical efforts grow substantially with the total number of mesh points used for the representation of the desired function. Moreover, they quickly grow together with the order number of a mesh point inside the same mesh.

In this section, we suggest an algorithm for the numerical solution of the first kind of Volterra integro-differential equation. The essence of the algorithm is based on the *recurrent* property of the function $\gamma(r)$: for a given set of mesh points $(r_1 = 0, \ldots, r_n = r, r_{n+1} = r + \delta r, \ldots)$ for the calculation of $\gamma_{n+1} = \gamma(r + \delta r)$ one needs to integrate over all values of γ, calculated at the previous n points. It is this integration which comprises the main difficulty of the numerical solution and makes the main difference to the local potential case. We develop the approximate scheme, in which the calculation of the $(n + 1)$th point requires only the information, stored on the nth step, *and* few additional algebraic operations. Under this condition, the numerical efforts for local and non-local problems become comparable.

We start by considering the integrals

$$J[r] \equiv \int_0^r \mathrm{d}r'\, V_\ell(r, r') \exp\left\{-\int_{r'}^r Q(s)\,\mathrm{d}s\right\} \tag{24}$$

and

$$J[r+\delta r] \equiv \int_0^{r+\delta r} \mathrm{d}r'\, V_\ell(r+\delta r, r') \exp\left\{-\int_{r'}^{r+\delta r} Q(s)\,\mathrm{d}s\right\} \tag{25}$$

where

$$Q(s) = \frac{\sin\gamma(s)\dot{q}(\kappa s) + \cos\gamma(s)\dot{p}(\kappa s)}{\sin\gamma(s)q(\kappa s) + \cos\gamma(s)p(\kappa s)}. \tag{26}$$

Our aim is to express $J[r+\delta r]$ through $J[r]$, r and δr. For the numerical estimation of the integrals below, we use the rectangular scheme with an arbitrary mesh, which gives the integral value with the numerical error of the second order in δr:

$$\int_{r_1}^{r_N} f(r)\,\mathrm{d}r = (f_1 + f_2 + \cdots + f_{N-1})\delta r + \max_{x\in[r_1,r_N]} |f'(x)| \frac{(N-1)(\delta r)^2}{2}. \tag{27}$$

The simplicity of the rectangular scheme, without loss of generality, allows us to clarify the calculation procedure, described below. Of course, the application of higher-order integration schemes would increase the accuracy of this procedure.

For the exponent from equation (25) we write

$$\exp\left\{-\int_{r'}^{r+\delta r} Q(s)\,\mathrm{d}s\right\} = \exp\left\{-\int_{r'}^{r} Q(s)\,\mathrm{d}s\right\} \exp\left\{-\int_{r}^{r+\delta r} Q(s)\,\mathrm{d}s\right\}.$$

The last factor does not contain r' and it is equal to

$$\exp\left(-Q(r)\delta r + \max_{x\in[r,r+\delta r]} |-Q'(x)| \frac{(\delta r)^2}{2}\right)$$
$$= \exp\left(-Q(r)\delta r\right)\left(1 + \max_{x\in[r,r+\delta r]} |Q'(x)| \frac{(\delta r)^2}{2} + \cdots\right).$$

Hence, the target integral (25) approximately equals

$$J[r+\delta r] \simeq \exp(-Q(r)\delta r) \int_0^{r+\delta r} \mathrm{d}r'\, V(r+\delta r, r') \exp\left\{-\int_{r'}^{r} Q(s)\,\mathrm{d}s\right\} \tag{28}$$

with the upper value of the second-order error R_{exp}:

$$R_{\mathrm{exp}} \leqslant \max_{x\in[r,r+\delta r]} |Q'(x)| \frac{(\delta r)^2}{2} \times \max_{x\in[0,r+\delta r]} |J(x)|. \tag{29}$$

In the same way, the integral in equation (28) can be divided into two parts, namely

$$\int_0^{r} \mathrm{d}r'\, V(r+\delta r, r') \exp\left\{-\int_{r'}^{r} Q(s)\,\mathrm{d}s\right\}$$
$$+ \int_r^{r+\delta r} \mathrm{d}r'\, V(r+\delta r, r') \exp\left\{-\int_{r'}^{r} Q(s)\,\mathrm{d}s\right\}. \tag{30}$$

The second term of this expression is approximated up to the error R_{int}

$$R_{\mathrm{int}} \leqslant \max_{x\in[r,r+\delta r]} \left|\frac{\partial V(r+\delta r, x)}{\partial x}\right| \frac{(\delta r)^2}{2} \tag{31}$$

by

$$\int_r^{r+\delta r} \mathrm{d}r'\, V(r+\delta r, r') \exp\left\{-\int_{r'}^{r} Q(s)\,\mathrm{d}s\right\}$$
$$\simeq \delta r\, V(r+\delta r, r) \exp\left\{-\int_{r}^{r} Q(s)\,\mathrm{d}s\right\} = \delta r\, V(r+\delta r, r). \tag{32}$$

The first term of equation (30)

$$\int_0^r \mathrm{d}r'\, V(r+\delta r, r') \exp\left\{-\int_{r'}^r Q(s)\,\mathrm{d}s\right\} \tag{33}$$

differs from $J[r]$ only in that the potential V is evaluated at the point $(r+\delta r, r')$ instead of (r, r'). This can be overcome in two different ways.

(1) Firstly, we perform the expansion of $V(r+\delta r)$ in Taylor series:

$$V(r+\delta r, r') \simeq V(r, r') + \frac{\partial V(r, r')}{\partial r}\delta r + \frac{1}{2}\frac{\partial^2 V(r, r')}{\partial r^2}\delta r^2 + \cdots. \tag{34}$$

The first terms yields the following approximate expression for $J[r+\delta r]$

$$J[r+\delta r] \simeq J[r]\,\mathrm{e}^{-Q(r)\delta r} + V(r+\delta r, r)\delta r. \tag{35}$$

For a complete account of all first order in δr terms for $J[r+\delta r]$ it is necessary to estimate the term with the first derivative of the potential:

$$J^{(1)}[r] \equiv \int_0^r \mathrm{d}r' \frac{\partial V(r, r')}{\partial r} \exp\left(-\int_{r'}^r Q(s)\,\mathrm{d}s\right). \tag{36}$$

This integral can be treated, in the same way as previously described for the case of equations (24)–(35), by calculation of their increments. For the term containing the first derivative we obtain

$$J^{(1)}[r] \simeq J^{(1)}[r-\delta r]\,\mathrm{e}^{-Q(r-\delta r)\delta r} + \left.\frac{\partial V(x, y)}{\partial x}\right|_{x,y=r} \delta r \tag{37}$$

$$J[r+\delta r] \simeq J[r]\,\mathrm{e}^{-Q(r)\delta r} + V(r+\delta r, r)\delta r + J^{(1)}[r-\delta r]\,\mathrm{e}^{-(Q(r-\delta r)+Q(r))\delta r}\delta r + \left.\frac{\partial V(x, y)}{\partial x}\right|_{x,y=r} \mathrm{e}^{-Q(r)\delta r}\delta r^2 \tag{38}$$

or in terms of finite differences we can write

$$J_{n+1} \simeq J_n\,\mathrm{e}^{-Q_n\Delta r_n} + \left(V_{n+1,n} + J^{(1)}_{n-1}\,\mathrm{e}^{-(Q_{n-1}+Q_n)\Delta r_n}\right)\Delta r_n \qquad \Delta r_n = r_{n+1} - r_n. \tag{39}$$

As can be seen from the structure of the equations (35) and (38), accounting for terms in the potential expansion up to those containing the first derivative implies an accuracy of the calculation of $J[r+\delta r]$ of the first order in δr with the numerical error of the second order.

(2) The second way is useful when the potential is a product of two parts, separately depending on r and r': $V(r, r') = U(r)W(r')$. In this case the finite-difference scheme becomes exact, since we can write

$$J_{n+1} = \frac{U_{n+1}}{U_n} J_n \exp(-Q_n\Delta r_n) + U_{n+1}W_{n+1}\Delta r_n. \tag{40}$$

We conclude this part by noting the features of the finite-difference scheme based on equations (39) or (40): (i) it has a simple form; (ii) at each step, it reduces the integration to the calculation at one (the last) point; (iii) it can be directly used for the numerical implementation and built into the standard packages of the numerical solution of the ordinary differential equations. This finite-difference scheme corresponds to the first-order integration method, but based on the same idea it can be easily generalized to the next order methods with the higher integration accuracies.

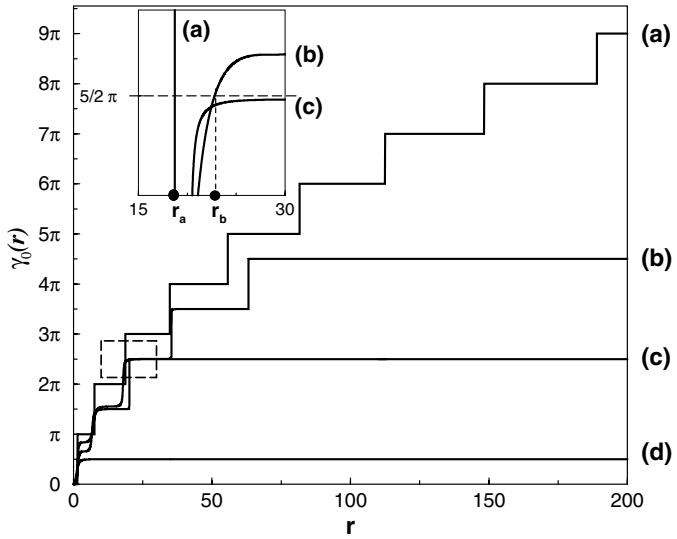

Figure 2. Function $\gamma_0(r)$ for different negative energies for the attractive Coulomb potential: (*a*) $E = -0.5 \times 10^{-10}$; (*b*) $E = -0.01$; (*c*) $E = -0.0556$; (*d*) $E = -0.5$ (energies are given in Hartree). The inset shows the behaviour of $\gamma_0(r)$ in the vicinity of $\gamma_0(r) = \frac{5}{2}\pi$.

5. Examples

To illustrate the method, we consider the SA function $\mathcal{F}_0(r)$ for zero orbital momentum ($\ell = 0$). As the simplest physical systems, we study a neutral atom and a negative hydrogen ion.

In figure 1 the physical meaning of the function $\gamma_0(r) = \arctan(\kappa\mathcal{F}_0(r))$ is illustrated for the attractive Coulomb potential for a particle with the energy $E = -0.0556$ Hartree. The integration of equation (23) (together with the initial condition this equation forms a Cauchy problem) is performed from $r = 0$ to $r = \infty$. The original potential $V(r) = -1/r$ is non-zero everywhere (see upper plot) and affects the derivative of $\gamma_0(r)$ along the whole radial axis. The asymptotic value of the arctangent of the SA function gives the arctangent of the SA: $\gamma_0(\infty) = \widehat{\gamma_0} = \arctan\widehat{\mathcal{F}_0}$. For the potential cut-off at R, the value of the derivative of $\gamma_0(r)$ is zero from R to ∞, and the value of the function $\gamma_0(r)$ coincides with the asymptotic value $\widehat{\gamma_0}^{(R)} \equiv \gamma_0(\infty) = \gamma_0(R)$ (see lower plot).

The behaviour of $\gamma_0(r)$ for the different energies (plots (*a*)–(*d*)) is shown in figure 2. The *ns* eigenstate with a given energy appears when the value of the function $\gamma_0(r)$ becomes equal to $(n - 1/2)\pi$. If this occurs at a finite distance R, then this eigenstate is associated with the cut-off potential $V^{(R)}$. If this distance is infinite, the eigenstate corresponds to a genuine potential. The blow-up of the vicinity of $\gamma_0(r) = \frac{5}{2}\pi$ is depicted in the inset: in cases (*a*) and (*b*) the eigenstate arises at the finite distance $r_a(r_b)$; in case (c) γ_0 will reach $\frac{5}{2}\pi$ at the infinity (therefore E_c is the energy of the 3*s*-state of the original Coulomb potential); the energy E_d will never be the 3*s*-eigenenergy of any (cut-off or genuine) Coulomb potential. Indeed, E_d is a ground-state energy of the latter and $\gamma_0(r, E_d)$ reaches the value $\pi/2$ at the infinity.

Finally, we consider the case of the non-local mean-field potential for the case of a negative hydrogen ion, arising on the first step of the Hartree–Fock self-consistent procedure. We suppose one electron occupies the 1s-state and the other—some other s-state, i.e. a hydrogen ion—is excited (this choice is made solely for the simplicity of the potentials). The Slater

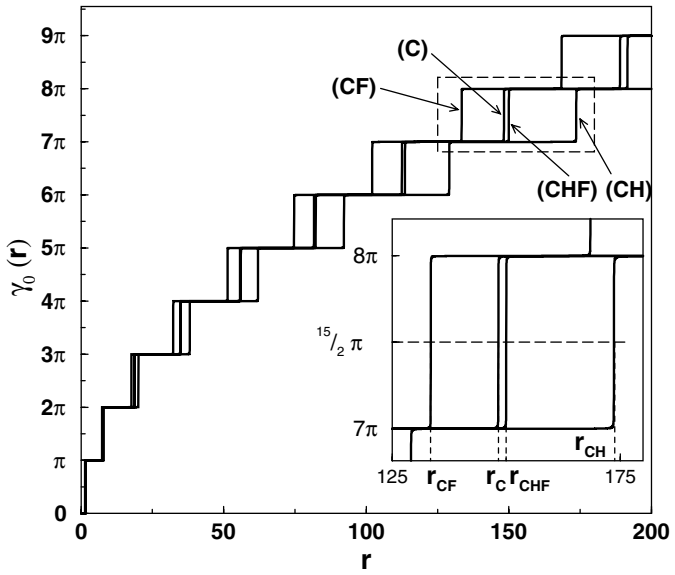

Figure 3. Function $\gamma_0(r)$ for local $V_C = -1/r$, and for different non-local potentials $V_{\rm CF}, V_{\rm CH}, V_{\rm CHF}$ (for an explanation, see the text). In all cases, the energy is the same: $E = -0.5 \times 10^{-10}$. The inset shows the behaviour of $\gamma_0(r)$ in the vicinity of $\gamma_0(r) = \frac{15}{2}\pi$.

expansion of the inter-electron interaction reads $\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{r}\sum_{\lambda=0}^{\infty}\left(\frac{r'}{r}\right)^{\lambda} P_\lambda(\cos(\widehat{\mathbf{r}\mathbf{r}}'))$. Together with the non-local density of a 1s-electron $\rho(r,r') = \frac{1}{4\pi}\exp(-2r') - \frac{1}{4\pi}\exp(-r)\exp(-r')$ and with the selection rule $\int_{-1}^{1} P_\ell(\cos(\widehat{\mathbf{r}\mathbf{r}}'))P_\lambda(\cos(\widehat{\mathbf{r}\mathbf{r}}'))\,\mathrm{d}(\widehat{\mathbf{r}\mathbf{r}}') = \delta_{\ell\lambda}$, which leaves only one term in the Slater expansion, it gives the non-local potential for the ns-electron $W = \frac{1}{r}[\exp(-2r') - \exp(-r)\exp(-r')]$. In figure 3 we explore the role of the non-locality as introduced by the potentials $V_F = -\frac{1}{4\pi}\exp(-r)\exp(-r')$ and $V_H = \frac{1}{4\pi}\exp(-2r')$ corresponding to the Fock and Hartree terms, respectively. We depict function $\gamma_0(r)$ for the bare Coulomb electron–ion interaction (C), Coulomb plus Fock term (CF), Coulomb plus Hartree term (CH), and all three terms together (CHF). The inset shows the corresponding cut-off distances, at which these potentials acquire the eighth s-state $\left(\gamma_0(r) = \frac{15}{2}\pi\right)$. The smaller this distance is, the larger the strength of the potential. The strongest is the potential $V_{\rm CF}$, which contains two attractive terms, followed by the bare Coulomb potential. Slightly more shallow is the total potential $V_{\rm CHF}$, containing two attractive and one repulsive terms. This is reflected, for example, in the extrusion of the highest Coulomb bound states in the continuum when the inter-electron interaction is switched on. The most weak is $V_{\rm CH}$, lacking the attractive exchange term.

6. Conclusions

In this paper, we have employed the well-established concept of the variable-phase approach for the description of a non-relativistic quantum particle in a non-local potential. To obtain simultaneously the bound and the scattering states, we have derived an integro-differential equation for the determination of the SA. Furthermore, we have proposed a fast numerical scheme for the solution of such integro-differential equations and we have demonstrated that the algorithm involves numerical efforts that are of the same order as for local potentials.

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Appendix

We start from the Schrödinger equation for the radial wavefunction u

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}u_\ell(r) + \left(k^2 - \frac{\ell(\ell+1)}{r^2}\right)u_\ell(r) = \int_0^\infty \mathrm{d}r'\, V_\ell(r,r')u_\ell(r') \tag{A.1}$$

and we make the replacement $u \to \alpha, \delta$ (the label for the orbital momentum is omitted for brevity)

$$\left\{\begin{array}{l} u = \alpha F \\ \frac{\mathrm{d}\alpha}{\mathrm{d}r}F = \alpha\frac{\mathrm{d}\delta}{\mathrm{d}r}G \end{array}\right| \qquad \text{where} \quad \begin{array}{ll} \alpha \equiv \alpha_\ell(r), \delta \equiv \delta_\ell(r) & \text{new functions} \\ j \equiv j_\ell(kr), n \equiv n_\ell(kr) & \text{Riccati–Bessel functions} \\ F = j\cos\delta - n\sin\delta & \text{auxiliary} \\ G = j\sin\delta + n\cos\delta & \text{functions} \end{array}. \tag{A.2}$$

Using the identity

$$\begin{aligned}\frac{\mathrm{d}F}{\mathrm{d}r} &= \frac{\mathrm{d}}{\mathrm{d}r}\left[j\cos\delta - n\sin\delta\right] = \left[\frac{\mathrm{d}j}{\mathrm{d}r}\cos\delta - j\sin\delta\frac{\mathrm{d}\delta}{\mathrm{d}r} - \frac{\mathrm{d}n}{\mathrm{d}r}\sin\delta - n\cos\delta\frac{\mathrm{d}\delta}{\mathrm{d}r}\right] \\ &= \left[\frac{\mathrm{d}j}{\mathrm{d}r}\cos\delta - \frac{\mathrm{d}n}{\mathrm{d}r}\sin\delta\right] - \frac{\mathrm{d}\delta}{\mathrm{d}r}G \end{aligned} \tag{A.3}$$

we obtain the first derivative of u:

$$\frac{\mathrm{d}u}{\mathrm{d}r} = \frac{\mathrm{d}(\alpha F)}{\mathrm{d}r} = \alpha\frac{\mathrm{d}F}{\mathrm{d}r} + \frac{\mathrm{d}\alpha}{\mathrm{d}r}F = \alpha\frac{\mathrm{d}F}{\mathrm{d}r} + \alpha\frac{\mathrm{d}\delta}{\mathrm{d}r}G = \alpha\left[\frac{\mathrm{d}j}{\mathrm{d}r}\cos\delta - \frac{\mathrm{d}n}{\mathrm{d}r}\sin\delta\right] \tag{A.4}$$

The second derivative of u transforms to

$$\begin{aligned}\frac{\mathrm{d}^2u}{\mathrm{d}r^2} &= \frac{\mathrm{d}}{\mathrm{d}r}\left(\alpha\left[\frac{\mathrm{d}j}{\mathrm{d}r}\cos\delta - \frac{\mathrm{d}n}{\mathrm{d}r}\sin\delta\right]\right) = \frac{\mathrm{d}\alpha}{\mathrm{d}r}\left[\frac{\mathrm{d}j}{\mathrm{d}r}\cos\delta - \frac{\mathrm{d}n}{\mathrm{d}r}\sin\delta\right] \\ &\quad + \alpha\left[\frac{\mathrm{d}^2j}{\mathrm{d}r^2}\cos\delta - \frac{\mathrm{d}^2n}{\mathrm{d}r^2}\sin\delta\right] - \alpha\frac{\mathrm{d}\delta}{\mathrm{d}r}\left[\frac{\mathrm{d}j}{\mathrm{d}r}\sin\delta + \frac{\mathrm{d}n}{\mathrm{d}r}\cos\delta\right] \\ &= \alpha\frac{\mathrm{d}\delta}{\mathrm{d}r}\frac{G}{F}\left[\frac{\mathrm{d}j}{\mathrm{d}r}\cos\delta - \frac{\mathrm{d}n}{\mathrm{d}r}\sin\delta\right] + \alpha\left[\frac{\mathrm{d}^2j}{\mathrm{d}r^2}\cos\delta - \frac{\mathrm{d}^2n}{\mathrm{d}r^2}\sin\delta\right] \\ &\quad - \alpha\frac{\mathrm{d}\delta}{\mathrm{d}r}\left[\frac{\mathrm{d}j}{\mathrm{d}r}\sin\delta + \frac{\mathrm{d}n}{\mathrm{d}r}\cos\delta\right] = \alpha\frac{\mathrm{d}\delta}{\mathrm{d}r}\left(\frac{G}{F}\left[\frac{\mathrm{d}j}{\mathrm{d}r}\cos\delta - \frac{\mathrm{d}n}{\mathrm{d}r}\sin\delta\right]\right. \\ &\quad \left. - \left[\frac{\mathrm{d}j}{\mathrm{d}r}\sin\delta + \frac{\mathrm{d}n}{\mathrm{d}r}\cos\delta\right]\right) + \alpha\left[\frac{\mathrm{d}^2j}{\mathrm{d}r^2}\cos\delta - \frac{\mathrm{d}^2n}{\mathrm{d}r^2}\sin\delta\right] \\ &:= \alpha\frac{\mathrm{d}\delta}{\mathrm{d}r}\frac{W}{F} + \alpha\left[\frac{\mathrm{d}^2j}{\mathrm{d}r^2}\cos\delta - \frac{\mathrm{d}^2n}{\mathrm{d}r^2}\sin\delta\right]. \end{aligned} \tag{A.5}$$

Let us look at W

$$\frac{W}{F} = \frac{G}{F}\left[\frac{\mathrm{d}j}{\mathrm{d}r}\cos\delta - \frac{\mathrm{d}n}{\mathrm{d}r}\sin\delta\right] - \left[\frac{\mathrm{d}j}{\mathrm{d}r}\sin\delta + \frac{\mathrm{d}n}{\mathrm{d}r}\cos\delta\right]$$

$$= \frac{1}{F}\left(G\left[\frac{\mathrm{d}j}{\mathrm{d}r}\cos\delta - \frac{\mathrm{d}n}{\mathrm{d}r}\sin\delta\right] - F\left[\frac{\mathrm{d}j}{\mathrm{d}r}\sin\delta + \frac{\mathrm{d}n}{\mathrm{d}r}\cos\delta\right]\right)$$
$$= \frac{1}{F}\left(n\frac{\mathrm{d}j}{\mathrm{d}r} - j\frac{\mathrm{d}j}{\mathrm{d}r}\right)(\cos^2\delta + \sin^2\delta). \tag{A.6}$$

Thus, W is a Wronskian of the functions $n(kr)$ and $j(kr)$, and is equal to $-k$:

$$W = n\frac{\mathrm{d}j}{\mathrm{d}r} - j\frac{\mathrm{d}n}{\mathrm{d}r} = -k \tag{A.7}$$

Then the substitution of equation (A.5) into the Schrödinger equation gives

$$-\alpha\frac{\mathrm{d}\delta}{\mathrm{d}r}\frac{k}{F(\delta(r))} + \left\{\alpha\left[\frac{\mathrm{d}^2 j}{\mathrm{d}r^2}\cos\delta - \frac{\mathrm{d}^2 n}{\mathrm{d}r^2}\sin\delta\right] + \alpha\left(k^2 - \frac{\ell(\ell+1)}{r^2}\right)[j\cos\delta - n\sin\delta]\right\}$$
$$= \int_0^\infty \mathrm{d}r'\, V_\ell(r, r')\alpha(r')F(\delta(r')). \tag{A.8}$$

The expression in the curly brackets is equal to 0 as a solution of the free equation

$$\frac{\mathrm{d}\delta}{\mathrm{d}r} = -\frac{F(\delta(r))}{k}\int_0^\infty \mathrm{d}r'\, V_\ell(r, r')\frac{\alpha(r')}{\alpha(r)}F(\delta(r')). \tag{A.9}$$

The equation for the derivative of $\alpha(r)$ from the system (A.2) may be integrated when δ is known:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}r}F(\delta) = \alpha\frac{\mathrm{d}\delta}{\mathrm{d}r}G(\delta) \Rightarrow \frac{\alpha(r')}{\alpha(r)} = \exp\left(-\int_{r'}^{r}\mathrm{d}s\frac{\mathrm{d}\delta(s)}{\mathrm{d}s}\frac{G(\delta(s))}{F(\delta(s))}\right). \tag{A.10}$$

Hence, the equation for the derivative of $\delta(r)$ has the final form:

$$\frac{\mathrm{d}\delta(r)}{\mathrm{d}r} = -\frac{1}{k}F(r)\int_0^\infty \mathrm{d}r'\, V(r, r')F(r')\exp\left[-\int_{r'}^{r}\frac{\delta(s)}{\mathrm{d}s}\frac{G(s)}{F(s)}\mathrm{d}s\right]. \tag{A.11}$$

Substituting $V(r, r') = V(r')\delta(r - r')$ in equation (A.11), we obtain the equation, coinciding with the phase equation for the local potential [1, 2]:

$$\frac{\mathrm{d}\delta(r)}{\mathrm{d}r} = -\frac{V(r)}{k}F^2(r) = -\frac{V(r)}{k}[j\cos\delta - n\sin\delta]^2. \tag{A.12}$$

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