Dressing of zero-range potentials into realistic molecular potentials of finite range

*Sergey B. Leble, Dmitry V. Ponomarev**

Gdansk University of Technology, Theoretical Physics and Quantum Informatics department,

ul. Narutowicza 11/12, 80-223, Gdansk, Poland

Abstract

The zero-range potentials of the radial Schrodinger equation and their dressing are investigated. A sequence of Darboux transformations involving set of parameters yields solvable potentials of finite-range with physically meaningful properties. In particular, matching newly obtained potential to that resulted from ab-initio methods computations is done in terms of discrete and continuous spectrum parameters. The approach, being a companion to conventional quantum simulation methods, combines symbolical and numerical calculations and is expected to work the best for molecules with high spherical symmetry, typically fullerenes.

Keywords: Effective potentials, zero-range potentials, Darboux transformation, dressing method, fullerenes.

1 Introduction

In many situations heavy molecular computations can be simplified by using effective potentials making any relevant calculations easier. One of the simplest physically meaningful potential to treat is a point-potential and the corresponding approach that allows to grasp geometrical structure of an object neglecting real interaction details at low energies is the so-called zero-range potential (ZRP) method. The method has been well developed up to now [11, 4, 3, 2, 7, 10] and extended further into the generalized zero-range potential (gZRP) method that takes into account effects of higher spherical waves in scattering problem by matching data with those obtained from an experiment or other calculations [12, 13, 8, 15, 9, 14].

Within the framework of the present work, we focus on the ZRP approach and extend it by means of a dressing procedure in the form of Darboux transformation (DT) [9, 15]. Multiple application of DT with certain parameters

*Currently at McMaster University, Mathematics and Statistics department.

yields a potential of finite range that captures the discrete and continuum spectra properties and, thus, is believed to appropriately describe a molecule.

2 Darboux transformation and dressing of ZRP

Consider one-dimensional Sturm-Liouville equation

$$L\psi = \lambda\psi, \tag{1}$$

where

$$L = -\frac{d^2}{dx^2} + u(x). \tag{2}$$

Now we apply such algebraic-differential transformation (referred as Darboux transformation [6])

$$D = \frac{d}{dx} - \sigma(x) \tag{3}$$

that the transformed equation preserve the same form

$$L^{[1]}\psi^{[1]} = \lambda\psi^{[1]}, \tag{4}$$

where $\psi^{[1]} = D\psi$, $L^{[1]} = -\frac{d^2}{dx^2} + u^{[1]}(x)$ and the transformed potential is

$$u^{[1]}(x) = u(x) - 2\sigma'(x). \tag{5}$$

It is straightforward to check that

$$\sigma(x) = \frac{\Phi_1'}{\Phi_1} \tag{6}$$

with Φ_1 being a particular solution to the original equation, i.e. it satisfies

$$-\Phi_1'' + u(x)\Phi_1 = \lambda_1\Phi_1$$

for some λ_1.

It can be shown that in case of multiple application of the Darboux transformation, the expression (6) is generalized into

$$\sigma(x) = \frac{d}{dx}\left[\log W(\Phi_1, \ldots, \Phi_N)\right]$$

resulting in the following transformation of the potential

$$u^{[N]}(x) = u(x) - 2\frac{d^2}{dx^2}\left[\log W(\Phi_1, \ldots, \Phi_N)\right]. \tag{7}$$

Corresponding transformation of the solution is given by the Crum's formula [5, 17]

$$\psi^{[N]} = D^{[N]}\psi = \frac{W(\Phi_1, \ldots, \Phi_N, \psi)}{W(\Phi_1, \ldots, \Phi_N)}, \tag{8}$$

where W denote determinants of the Wronskian matrices.

In spherical geometry the Schrodinger equation

$$-\left(\psi'' + \frac{2}{r}\psi'\right) = k^2\psi, \tag{9}$$

with notation $\psi = \psi(r)$ can be brought to the form (1) eligible for direct application of obtained transformation formulas. Namely, performing substitution $\psi = \chi/r$, one readily obtains one-dimensional wave equation with respect to χ while the potential term remains zero.

Therefore, the formulas (7), (11) in spherical coordinates should be replaced with

$$u^{[N]}(r) = -2\frac{d^2}{dr^2}\left[\log W(r\Phi_1, \ldots, r\Phi_N)\right] \tag{10}$$

and

$$\psi^{[N]} = D^{[N]}\psi = \frac{W(r\Phi_1, \ldots, r\Phi_N, r\psi)}{rW(r\Phi_1, \ldots, r\Phi_N)}. \tag{11}$$

Following an idea of the previous work [15, 9], we state that application of DT to the spherical Bessel function as seed solution

$$\psi_0(r) = j_0(kr) = \sin(kr)/(kr) \tag{12}$$

with the Hankel function as prop function

$$\Phi_0(r) = h_0^{(1)}(-i\kappa_0 r) = \exp(\kappa_0 r)/(\kappa_0 r) \tag{13}$$

results in ZRP behavior of the transformed solution $\psi_0^{[1]}(r)$

$$\psi^{[0]}(r) \equiv \psi_0^{[1]}(r) = C\left[s_0 h_0^{(1)}(kr) - h_0^{(2)}(kr)\right], \tag{14}$$

$$u_0^{[1]}(r) = 0. \tag{15}$$

Obtained ZRP with characteristic κ_0 being a pole $k = i\kappa_0$ of scattering matrix $s_0 = -\frac{(k+i\kappa_0)}{(k-i\kappa_0)}$ can be represented

as boundary condition

$$\left.\frac{d\log(r\psi)}{dr}\right|_{r=0} = -\kappa_0 = -1/a_0 \tag{16}$$

with a_0 termed as scattering length.

Next application of DT to (14) choosing prop function as

$$\Phi_1(r) = A_1 h_0^{(1)}(-i\kappa_1 r) + B_1 h_0^{(2)}(-i\kappa_1 r) \tag{17}$$

yields potential of finite range

$$u^{[1]}(r) \equiv u_0^{[2]}(r) = -2\frac{d^2}{dr^2}\log\left[r\Phi_1(r)\right] \tag{18}$$

As it follows from the Crum's formula (11), the transformed solution $\psi_0^{[2]}$ has behavior similar to (14) but only asymptotically

$$\psi^{[1]}(r) \underset{r\to\infty}{\approx} C\left[s_0^{[1]} h_0^{(1)}(kr) - h_0^{(2)}(kr)\right] \tag{19}$$

while scattering matrix $s_0^{[1]} = \frac{(k+i\kappa_0)(k+i\kappa_1)}{(k-i\kappa_0)(k-i\kappa_1)}$ contains one more pole $k = i\kappa_1$.

We note that value of normalization constant here is not the same as in (14), since we use C to denote generic constant which value is not of particular importance.

Instead of single DT, one may perform chain of N consecutive DTs applied to the ZRP solution (14) with prop functions

$$\Phi_m(r) = A_m h_0^{(1)}(-i\kappa_m r) + B_m h_0^{(2)}(-i\kappa_m r), \qquad m = 1, \ldots, N. \tag{20}$$

The solution transforms according to (11) and asymptotical expansion still has the same form as (19)

$$\psi^{[N]}(r) \underset{r\to\infty}{\approx} C\left[s_0^{[N]} h_0^{(1)}(kr) - h_0^{(2)}(kr)\right] \tag{21}$$

with $s_0^{[N]} = (-1)^{N+1}\frac{(k+i\kappa_0)(k+i\kappa_1)\cdot\ldots\cdot(k+i\kappa_N)}{(k-i\kappa_0)(k-i\kappa_1)\cdot\ldots\cdot(k-i\kappa_N)}$.

Thus, using DT we may add scattering matrix poles $k = i\kappa_m$ lying on positive imaginary k-semiaxis (i.e. $\kappa_m > 0$) corresponding to the bounded states of the molecule that we consider as known (or may be found by solving discrete spectrum problem using ZRP formulation).

This tranformation yields finite range N-dressed potential according to the general expression (10).

We note that although the scattering matrix $s_0^{[N]}$ in (21) is independent of choice of constants A_m, B_m, $m = 1, \ldots, N$, these constants (namely, the ratios A_m/B_m) affect singular behavior of transformed solution at the origin. This modifies conventional ZRP boundary condition (16)

$$\left.\frac{d\log(r\psi)}{dr}\right|_{r=0} = \left(\frac{d}{dr}\frac{W(r\Phi_1, \ldots, r\Phi_N, r\psi)}{W(r\Phi_1, \ldots, r\Phi_N)}\right) \Big/ \left.\frac{W(r\Phi_1, \ldots, r\Phi_N, r\psi)}{W(r\Phi_1, \ldots, r\Phi_N)}\right|_{r=0} = \text{const} \tag{22}$$

In particular case $N = 1$, $A_1 = B_1$, this modification reads [9]

$$\left.\frac{d\log(r\psi)}{dr}\right|_{r=0} = \frac{k^2+\kappa_1^2}{\kappa_0} \tag{23}$$

3 Application

In order to obtain analytical potential well describing a molecular structure, we apply the dressing method as described in the previous section choosing parameters of prop functions (20) in a way that obtained potential (10) must be physically meaningful.

As it was mentioned, spectral parameters κ_m, $m = 0, \ldots, N$ might be chosen according to the discrete spectrum of the molecule.

The choice of constants A_m, B_m, $m = 1, \ldots, N$ gives freedom to tune dressed potential to that obtained from "ab initio" calculations. However, one should be aware that certain proportion of these constants leads to a singular behavior at particular $r > 0$ that we consider unreasonable and should be eliminated. Namely, for a single Darboux transformation this consideration leads to the restriction $B_1/A_1 \geq -1$.

Adjusting dressed potential can be done by matching partial shifts η_l governing continuous spectrum solutions. In the Born approximation we have [18]

$$\eta_l \approx -\frac{2\mu}{\hbar^2}k\int_0^\infty j_l^2(kr)U(r)r^2dr. \tag{24}$$

Hence, in this case, the problem of matching phase shifts resorts to consequent minimization of functions at high values of k and large l (such that the Born approximation is valid)[1]

$$F_l\left(A_1, B_1, \ldots, A_N, B_N\right) = \frac{2\mu}{\hbar^2}k\left|\int_0^\infty j_l^2(kr)\left[U(r)-u^{[N]}(r)\right]r^2dr\right| \tag{25}$$

where $U(r)$ is averaged radial potential obtained from "ab initio" computations.

Evidently, the best results should be obtained for nearly isotropic molecules for which averaging over angles to obtain radial potential is the most reasonable. Typical examples of these structures are fullerenes and such averaged radial potential was dealt with in [16].

As an example of application of described dressing procedure, on the Fig. 1 we demonstrate finite range solvable potential obtained for the following set of parameters: $\kappa_1 = 1.66$, $\kappa_2 = 1.57$, $\kappa_3 = 1.39$, $\kappa_4 = 1.29$, $A_1 = -2$, $B_1 = -5$, $A_2 = 1$, $B_2 = 4$, $A_3 = -3$, $B_3 = 2$, $A_4 = 7$, $B_4 = 9$.

[1] There is no contradiction with low-energy assumption of the ZRP model, since here we already consider a potential of finite range.

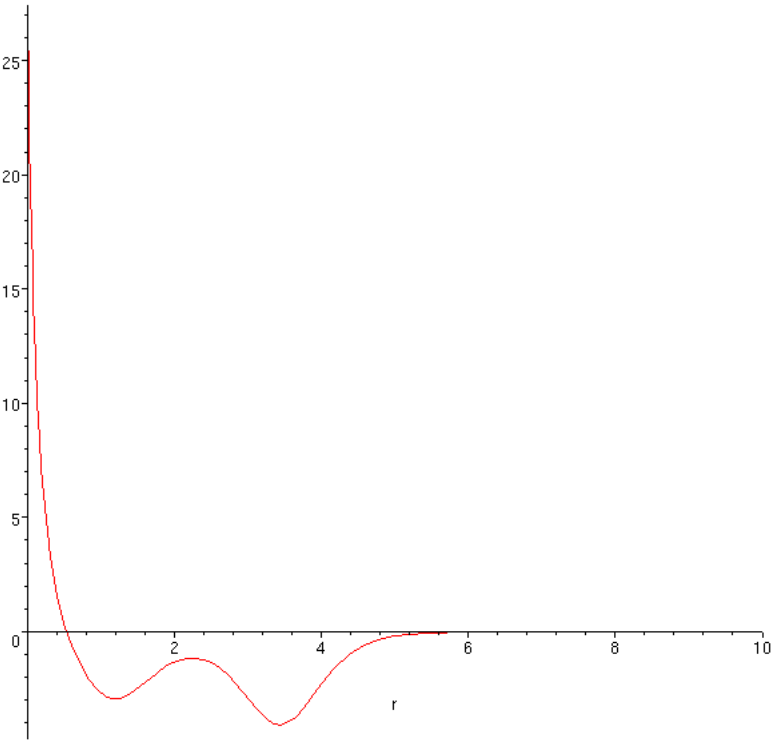

Fig. 1: An example of solvable finite range potential obtained by dressing procedure

4 Conclusions

The approach described in the present work offers an alternative to gZRP description. Final potential obtained by chain of DT applied to ZRP is of finite range and may be adjusted to possess physically meaningful properties. This can be achieved by matching discrete spectrum levels and partial waves phase shifts with those obtained by "ab initio" computational methods. Obtained in such way effective potential, preserving spectral structure of the molecule, can be used in further calculations where material constituents are molecules, not atoms, that will significantly simplify computation cost.

The algorithm is expected to be beneficially applied for isotropic molecules. Typical application might be description of fullerenes.

References

[1] Abramowitz M., Stegun I., "Handbook of mathematical functions with formulas, graphs, and mathematical tables", Dover, New York, 1964.

[2] Albeverio S., Gesztesy F., Hoegh-Krohn R., Holden H., "Solvable models in quantum mechanics", Springer, New York, 1988.

[3] Baz' A. I., Zel'dovich Ya. B., Perelomov A. M., "Scattering, reactions, and decays in nonrelativistic mechanics" (in Russian), Nauka, Moscow, 1971.

[4] Breit G., "The scattering of slow neutrons by bound protons: methods of calculation", Phys. Rev., 71, 215, 1947.

[5] Crum M.M., "Associated Sturm-Liouville systems", Quart. J. Math. Oxford Ser. (2), 6, 121–127, 1955.

[6] Darboux G., "Sur une proposition relative aux équations linéaires", C. R. Acad. Sci Paris, 94, 1456-1459, 1882.

[7] Demkov Yu. N., Ostrovskii V. N., "Zero-range potentials and their applications in atomic physics", Plenum Press, New York, 1988.

[8] Derevianko A., "Revised Huang-Yang multipolar pseudopotential", Phys. Rev. A, 72, 044701, 2005.

[9] Doktorov E. V., Leble S. B., "A dressing method in mathematical physics", Springer, London, 2006.

[10] Drukarev G., "The zero-range potential model and its application in atomic and molecular physics", Adv. Quantum Chem., 11, 251-274, 1979.

[11] Fermi E., "Sopra lo spostamento per pressione delle righe elevate delle serie spettrali", Il Nuovo Cimento, 11, 157-166, 1934.

[12] Huang K., "Statistical mechanics", Wiley, New York, 1963.

[13] Huang K., Yang C.N., "Quantum-mechanical many-body problem with hard-sphere interaction", Phys. Rev., 105, 767-775, 1957.

[14] Idziaszek Z., Callarco T., "Pseudopotential method for higher partial wave scattering", Phys. Rev. Lett., 96, 013201, 2006.

[15] Leble S. B., Yalunin S., "A dressing of zero-range potentials and electron–molecule scattering problem at low energies", Phys. Lett. A, 339, 83-88, 2005.

[16] Madjet M. E., Chakraborty H. S., Manson S. T., "Giant Enhancement in Low Energy Photoemission of Ar Confined in C60", Phys. Rev. Lett., 99, 243003, 2007.

[17] Matveev V. B., Salle M. A., "Darboux transformations and solitons", Springer-Verlag Berlin, Heidelberg, 1991.

[18] Messiah A., "Quantum mechanics", North-Holland Publishing Company, The Netherlands, 1961.