GREEN'S FUNCTION FOR THE ONE OF MODEL TWO-CENTRE POTENTIAL IN MOLECULAR PHYSICS

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The expansions of a Green's function for the Simmons molecular potential (SMP) over spheroidal function are built. The solutions of a degenerate hypergeometric equation are used as basis function system while expanding regular and irregular model spheroidal functions into series. Rather simple three-terms recurrence relations are obtained for the coefficients of these expansions.

1. Introduction

In the theory of electronic structure and spectra of molecular systems Green's function for the two-centre potential $V(\vec{r},R)$

$$\left[-\frac{1}{2}\Delta+V(\vec{r},R)-E(R)\right]G_E(\vec{r},\vec{r}\,';R)=\delta(\vec{r}-\vec{r}\,'), \tag{1}$$

plays fundamental role, similar to that of the one-centre Coulomb Green's function in the atomic structure theory. However, even for the simplest model - a problem of two purely Coulomb centres Z_1eZ_2 considered in Ref. [1] no closed analytical expression for the $G_E(\vec{r},\vec{r}\,';R)$ similar, e. g. to the well-known Hostler and Pratt expression [2], has been obtained. The expansions of the Green's function $G_E(\vec{r},\vec{r}\,';R)$ over partial waves have been constructed only in the separate case of molecular hydrogen ion H_2^+ [3], where the recurrent scheme of coefficient determination, related to cumbersome calculations were proposed.

More essentials for the perturbation theory problems, based on the usage of the Green's function approach, is the extension of methods, developed for the Z_1eZ_2 problem, to more complicated multielectron diatomic systems. In the modern theory of electron structure of complex molecules the self-consistent field method and the effective potential concept overcome these difficulties.

In our works the expansions of the Green's function for the two-centre potential model, suggested in Ref. [6] over spheroidal functions are built. While regular and irregular model spheroidal functions (MSFs) being expanded into series, the solutions Φ and Ψ of a degenerate hypergeometric equation [8], providing the required asymptotic behaviour of the MSFs at small intercentre distances ($R\to 0$), are used as basis functions.

2. Green's Function Expansions over Spheroidal Functions

Without concentrating here upon the possible versions of construction of the model potentials, and bearing in mind diatomic homonuclear systems with a single optical electron, we shall describe the interaction of the valence electron with the molecular core by a non-local model potential of the form [6]

$$V_{mod}(\vec{r},R)=-\frac{Z}{r_1}-\frac{Z}{r_2}+\sum_{m,\ell}\frac{B_{m\ell}(E,R)}{2r_1r_2}\hat{P}_{m\ell}\,, \tag{2}$$

where r_1, r_2 are the distances from the electron to the force centres 1 and 2, located at the distance R from each other; $\hat{P}_{m\ell}$ are the operators of projection onto the subspace of states with certain values of the orbital ℓ and magnetic m quantum numbers, and Z is the effective charge of each of the atomic (ionic) fragments – the constituents of the fragments of the two-centre system. The empirical parameters $B_{m\ell}(E,R)$ are chosen by the comparison of the calculated lowest level (term) E of the valence electron with the given ℓ and m with its experimental value. The potential (2) is the generalization of the well-known in atomic physics Simmons model potential [9] to the molecular case and goes over into it in the limit of the united atom ($R \to 0$). The unique feature of the model potential (2) is the possibility of separation of variables in the Schroedinger equation in prolate spheroidal coordinates ξ, η, φ [1] which enables the exact calculation of terms and electron wave functions.

Let us to represent Green's function $G_E(\vec{r},\vec{r}\,';R)$ in the form of an expansion over a complete orthonormalized system of oblate angular spheroidal functions $\overline{S}_{m\ell}(p,\eta)$ [1]:

$$G_E(\vec{r},\vec{r}\,';R) \equiv G_E(\xi,\eta,\varphi;\xi',\eta',\varphi'|R) = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} G_{m\ell}(\xi,\xi';E)\overline{S}^{*}_{m\ell}(p,\eta)\overline{S}_{m\ell}(p,\eta')\frac{e^{im(\varphi-\varphi')}}{2\pi}, \tag{3}$$

By substituting the expansion (3) into equation (1), having been written in the prolate spheroidal coordinates, and separating the angular variables η and φ, we obtain a differential equation for the radial part of the Green's function $G_{m\ell}(\xi,\xi';E)$:

$$\left\{\frac{d}{d\xi}\left[\left(\xi^2-1\right)\frac{d}{d\xi}\right]+\left[-A_{m\ell}-p^2\left(\xi^2-1\right)+2p\alpha\xi-\frac{m^2}{\xi^2-1}\right]\right\}G_{m\ell}(\xi,\xi';E) = -\frac{4}{R}\delta(\xi-\xi'), \tag{4}$$

where $p=\frac{1}{2}R(-2E)^{1/2}$, $\alpha = 2Z(-2E)^{-1/2}$, $A_{m\ell}(E,R)=\lambda_{m\ell}\left(p^2\right)+B_{m\ell}(E,R)$, and $\lambda_{m\ell}$ denote the eigenvalues of the angular problems, corresponding to the oblate spheroidal functions $\overline{S}_{m\ell}(p,\eta)$ [1]. Thus, the function $G_{m\ell}(\xi,\xi';E)$ is the Green's function of a one-dimensional radial motion and is conventionally expressed by two linearly independent solutions $\Pi^{(1)}_{m\ell}(p,\xi)$ and $\Pi^{(2)}_{m\ell}(p,\xi)$ of the homogeneous part of equation (4). The solution $\Pi^{(1)}_{m\ell}(p,\xi)$ is regular at $\xi \to 1$ and divergent at infinity, and $\Pi^{(2)}_{m\ell}(p,\xi)$ is, contrary, divergent at $\xi \to 1$ and regular at infinity. Let us to introduce the new independent variables and new sought functions in equation (4) according to the formulae

$$\widetilde{\Pi}^{(\pm)}_{m\ell}(x_\pm)=\left(\frac{\xi\pm 1}{\xi\mp 1}\right)^{m/2}\Pi_{m\ell}(p,\xi),\ \ x_\pm = p(\xi\pm 1),\ \ \left(2p\le x_+<\infty,\quad 0\le x_- <\infty\right). \tag{5}$$

Hereinafter the upper signs are related to $\widetilde{\Pi}^{(+)}_{m\ell}(x_+)$ and the lower ones – to $\widetilde{\Pi}^{(-)}_{m\ell}(x_-)$. By the transformation (5) homogeneous part of the equation (4) is reduced to two separate equations for $\widetilde{\Pi}^{(\pm)}_{m\ell}(x_\pm)$:

$$\begin{aligned}&\left[\frac{d}{dx_\pm}\left(x_\pm^2\frac{d}{dx_\pm}\right)-x_\pm^2+2\alpha x_\pm-\nu(\nu+1)\right]\widetilde{\Pi}^{(\pm)}_{m\ell}(x_\pm)+\\ &+\frac{p}{x_\pm\mp 2p}\left[\pm 2(m+1)x_\pm\frac{d}{dx_\pm}+\left(\frac{\nu(\nu+1)-A_{m\ell}}{p}\pm 2\alpha\right)x_\pm\mp 2\nu(\nu+1)\right]\widetilde{\Pi}^{(\pm)}_{m\ell}(x_\pm)\equiv\\ &\equiv T_\nu(x_\pm)\widetilde{\Pi}^{(\pm)}_{m\ell}(x_\pm)+pQ_\pm(x_\pm)\widetilde{\Pi}^{(\pm)}_{m\ell}(x_\pm)=0,\end{aligned} \tag{6}$$

where the parameter $\nu \equiv \nu_{m\ell}(E,R)$ is given by $\nu = -\frac{1}{2}+\frac{1}{2}\sqrt{1+4B_{m\ell}(E,0)+4\ell(\ell+1)}$. When p tends to zero, both equations of (6) go over into one $T_\nu R(x)=0$ $\left(0\le x<\infty\right)$, whose two independent solutions are the functions $R_\nu^{(1)}(x)$ and $R_\nu^{(2)}(x)$ expressed directly in terms of regular Φ and irregular Ψ solutions of a degenerate hypergeometric equation [8]:

$$R_\nu^{(1)}(x) \equiv x^\nu e^{-x}\Phi(-\alpha+\nu+1, 2\nu+2, 2x), \qquad R_\nu^{(2)}(x) \equiv x^\nu e^{-x}\Psi(-\alpha+\nu+1, 2\nu+2, 2x). \tag{7}$$

The above speculations suggest the regular $\widetilde{\Pi}_{m\ell}^{(1,\pm)}(x_\pm)$ and the irregular $\widetilde{\Pi}_{m\ell}^{(2,\pm)}(x_\pm)$ solutions of each of the equations (6) to be given as the following infinite sums:

$$\widetilde{\Pi}_{m\ell}^{(1,\pm)}(x_\pm) = \sum_{s=0}^{\infty} h_s^{(\pm)}(p|\alpha, A_{m\ell}) R_{s+\nu}^{(1)}(x_\pm), \quad \widetilde{\Pi}_{m\ell}^{(2,\pm)}(x_\pm) = \sum_{s=0}^{\infty} \widetilde{h}_s^{(\pm)}(p|\alpha, A_{m\ell}) R_{s+\nu}^{(2)}(x_\pm), \tag{8}$$

here the expansion coefficients $h_s^{(\pm)}$ and $\widetilde{h}_s^{(\pm)}$ are to be determined. Having substituted these expansions into the corresponding equations (6) and having used the recurrent relations (See Refs. [5, 13]) for the basis functions $R_s^{(1)}(x)$ and $R_s^{(2)}(x)$, we obtain two infinite three-term systems of linear equations for the coefficients $h_s^\pm \equiv h_s^\pm(p|\alpha, A_{m\ell})$, $\widetilde{h}_s^\pm \equiv \widetilde{h}_s^\pm(p|\alpha, A_{m\ell})$:

$$\pm p\alpha_s h_{s-1}^{(\pm)} + (\beta_s - A_{m\ell}) h_s^{(\pm)} \mp p\gamma_s h_{s+1}^{(\pm)} = 0, \;\; s = 0,1,2\ldots, \;\; h_{-1}^{(\pm)} = 0, \tag{9}$$

$$\mp p\widetilde{\alpha}_s \widetilde{h}_{s-1}^{(\pm)} + (\widetilde{\beta}_s - A_{m\ell}) \widetilde{h}_s^{(\pm)} \pm p\widetilde{\gamma}_s \widetilde{h}_{s+1}^{(\pm)} = 0, \;\; s = 0,1,2\ldots, \;\; \widetilde{h}_{-1}^{(\pm)} = 0, \tag{10}$$

$$\alpha_s = \frac{2\left((s+\nu)^2 - \alpha^2\right)(s+\nu+m)}{(s+\nu)(2s+2\nu-1)(2s+2\nu+1)}, \; \beta_s = (s+\nu)(s+\nu+1), \; \gamma_s = 2(s+\nu+1)(s+\nu+1-m),$$

$$\widetilde{\alpha}_s = \frac{4(s+\nu-\alpha)(s+\nu+m)}{2s+2\nu-1}, \; \widetilde{\beta}_s = \beta_s, \; \widetilde{\gamma}_s = \frac{(s+\nu+\alpha+1)(s+\nu-m+1)}{2s+2\nu+3}. \tag{11}$$

The recurrent systems (9) ((10)) determine the coefficients $h_s^{(\pm)}$ ($\widetilde{h}_s^{(\pm)}$) within arbitrary factors, fixed by the conditions

$$\sum_{s=0}^{\infty} h_s^{(\pm)} \frac{\Gamma(2s+2\nu+2)}{2^{s+\nu}\Gamma(s+\nu+1-\alpha)} = 1, \quad \sum_{s=0}^{\infty} 2^{-s-\nu}\widetilde{h}_s^{(\pm)} = 1. \tag{12}$$

The expression for radial Green's function $G_{m\ell}(\xi,\xi';E)$ with the account of the Wronskian value (See Refs. [3, 7]) can now be given by

$$G_{m\ell}(\xi,\xi';E) = \frac{8Z}{\alpha}\left(\frac{x_\mp x'_\mp}{x_\pm x'_\pm}\right)^{m/2} \widetilde{\Pi}_{m\ell}^{(1,\pm)}(x_{\pm<}) \widetilde{\Pi}_{m\ell}^{(2,\pm)}(x_{\pm>}). \tag{13}$$

3. Limiting Values and Asymptotic Expansions of the Two-Centre Green's Function at Small Intercentre Distances

In many physical problems whose examples are considered in [1], the asymptotic of the Green's function $G_E(\vec{r},\vec{r}\,';R)$ at small values of the intercentre distance should be known. Hence the necessity of the asymptotic expansions of $S_{m\ell}(p,\eta)$, $\widetilde{\Pi}_{m\ell}^{(1,\pm)}(x_\pm)$ and $\widetilde{\Pi}_{m\ell}^{(2,\pm)}(x_\pm)$ functions over a small parameter p at the fixed quantum numbers ℓ and m to be constructed arises. We use an asymptotic method, proposed by Abramov and Slavyanov [13], to search for such expansions.

We begin with the oblate angular spheroidal function $S_{m\ell}(p,\eta)$. The expansion for normalized angular spheroidal functions can be written in a form:

$$\bar{S}_{m\ell}(p,\eta) = N_{m\ell}^{-1}(p) \sum_{n=Ent[(m-\ell)/2]}^{\infty} d_{2n+\delta}^{m\ell} P_{\ell+2n+\delta}^{m}(\eta); \quad \delta = \begin{cases} 0 & if \quad \ell - m = 2k, \\ 1 & if \quad \ell - m = 2k+1, \quad k = 0,1,2... \end{cases} \tag{14}$$

Here $P_\ell^m(\eta)$ - associated Legendre polynomials, $N_{m\ell}(p)$- normalize factor and Ent$[\rho]$ is the integer part of the real number ρ. The expansion coefficients $d_{2n+\delta}^{m\ell}$ fulfill the three-term recurrent relations [1]:

$$\begin{aligned} & p^2 B_{2n+\delta} B_{2n+1+\delta} d_{2n+2+\delta}^{m\ell} + \left[\lambda_\delta^{(\eta)} - (\ell+2n+\delta)(\ell+2n+1+\delta) - p^2 + \right. \\ & \left. + p^2 \left(B_{2n-1+\delta} E_{2n+\delta} + B_{2n+\delta} E_{2n+1+\delta}\right)\right] d_{2n+\delta}^{m\ell} + p^2 E_{2n+\delta} E_{2n-1+\delta} d_{2n-2+\delta}^{m\ell} = 0, \end{aligned} \tag{15}$$

$$B_k = \frac{\ell+k+m+1}{2\ell+2k+3}, \quad E_k = \frac{\ell+k-m}{2\ell+2k-1}, \quad d_{m-\ell-2+\delta}^{m\ell} = 0. \tag{16}$$

We search for the separation constant $\lambda_\delta^{(\eta)}$ and the expansion coefficients $d_{2n+\delta}^{m\ell}$ in the form of asymptotic series over the powers of a small parameter p^2:

$$\lambda_\delta^{(\eta)} = \sum_{j=0}^{\infty} [\lambda_\delta]_{2j} p^{2j}; \quad d_{2n+\delta}^{m\ell} = p^{|2n|} \sum_{j=0}^{\infty} \left[d_{2n+\delta}^{m\ell}\right]_{2j} p^{2j}, \quad d_\delta = 1. \tag{17}$$

By substituting these expansions consequently into each equation of the system (15), starting from $n=0$, and equating the coefficients at the equal powers of p^2 to zero, we obtain the recurrent relations to determine the expansion coefficients $\left[d_{2n+\delta}^{m\ell}\right]_{2j}$ and $[\lambda_\delta]_{2j}$. The chain of equations, corresponding to $n=0$, enables the $[\lambda_\delta]_{2j}$ values to be expressed in terms of $\left[d_{\pm 2+\delta}^{m\ell}\right]_{2j-4}$ coefficients. Some coefficients $[\lambda_\delta]_{2j}$ and $\left[d_{\pm 2+\delta}^{m\ell}\right]_{2j-4}$ are given below:

$$[\lambda_\delta]_0 = (\ell+\delta)(\ell+\delta+1), \quad [\lambda_\delta]_2 = 1 - \left(B_{-1+\delta} E_\delta + B_\delta E_{1+\delta}\right),$$

$$[\lambda_\delta]_4 = \frac{E_\delta E_{-1+\delta} B_{-1+\delta} B_{-2+\delta}}{2(2\ell+2\delta-1)} - \frac{B_\delta B_{1+\delta} E_{1+\delta} E_{2+\delta}}{2(2\ell+2\delta+3)},$$

$$[d_{2+\delta}]_0 = \frac{E_{1+\delta} E_{2+\delta}}{2(2\ell+2\delta+3)},$$

$$[d_{2+\delta}]_2 = \frac{E_{1+\delta} E_{2+\delta}}{4(2\ell+2\delta+3)^2} \left[B_{1+\delta} E_{2+\delta} + B_{2+\delta} E_{3+\delta} - B_{-1+\delta} E_\delta - B_\delta E_{1+\delta}\right].$$

In order to space saving we represented here the few coefficients of the expansion (17) only, but in the numerical calculation for ZeZ systems we keep up to ten coefficients en each expansion. We have checked the applicability of our approximate results with numerical solutions obtained for ZeZ systems in [4]. Some results are represented in table 1 and 2. For the sake of convenience while presenting the results, the values of separation constant are recalculated in the notation system chosen in Ref. [4]. In table 2 the values of the coefficients (See eq. (14)) calculated using asymptotic expansion (17) are compared with the numerical solution for them from [4]. The normalization for $d_{2n+\delta}^{m\ell}$ coefficients, accepted in [4] is used here.

Table 1. Separation constant $\lambda_{m\ell}^{(\eta)} - p^2$ of the angular equation for the oblate spheroidal function, $\lambda_{m\ell}^{(\eta)} - p^2 = \Lambda_{m\ell} \times 10^n$.

	This work		Ref. [4]		This work		Ref. [4]	
p	Λ_{00}	n	Λ_{00}	n	Λ_{01}	n	Λ_{01}	n
0.1	-3.33482	-3	-3.34	-3	1.99400	0	1.99400	0
0.3	-3.01203	-2	-	-	1.94594	0	-	-
0.6	-1.21942	-1	-1.2194	-1	1.78311	0	1.78311	0
0.9	-2.79963	-1	-	-	1.50953	0	-	-
1.5	-8.29869	-1	-8.2987	-1	6.16041	-1	6.1604	-1
2	-1.59451	0	-1.59449	0	-5.05240	-1	-5.0524	-1

Table 2. Expansion coefficients $d_{2n+\delta}^{m\ell}$ for the oblate angular spheroidal function calculated for the ground state ($\ell = 0$, $m = 0$), $d_r^{m\ell} = D_r \times 10^n$.

	This work		Ref. [4]		This work		Ref. [4]		This work		Ref. [4]	
p	D_0	n	D_0	n	D_2	n	D_2	n	D_4	n	D_4	n
0.1	1.0006	0	1.0006	0	1.1121	-3	1.1121	-3	1.9067	-7	1.9066	-7
0.3	1.0050	0	-	-	1.0079	-2	-	-	1.5562	-5	-	-
0.6	1.0205	0	1.0205	0	4.1281	-2	4.1283	-2	2.5558	-4	2.5555	-4
0.9	1.0478	0	-	-	9.6662	-2	-	-	1.3523	-3	-	-
1.2	1.0892	0	1.0892	0	1.8182	-1	1.8182	-1	4.5523	-3	4.5385	-3
1.5	1.1483	0	1.1484	0	3.0571	-1	3.0573	-1	1.2080	-2	1.1983	-2

The same approach can be applied to the studies of the asymptotic behavior of the regular and irregular radial MSFs at small values of the p parameter. The analytic representation for the coefficients of radial MSFs would be represented in our follow publications.

Concluding, we should note that an approach to solving the perturbation-theory nonlinear equations, related to the Timan-Schwarz method application, has been also discussed in the literature (See e. g. [10-12]). These approaches are formally equivalent, but the Green's function method possesses an advantage, being known in various fields of physics, universal in its applications

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ФУНКЦІЯ ГРІНА ДЛЯ ОДНОГО МОДЕЛЬНОГО ДВОЦЕНТРОВОГО ПОТЕНЦІАЛУ В МОЛЕКУЛЯРНІЙ ФІЗИЦІ

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Побудовано розклад для функції Гріна молекулярного потенціалу Саймонса за сфероїдальними функціями. При розкладанні регулярних і нерегулярних модельних сфероїдальних функцій в ряди в якості базисних систем використано розв`язки виродженого гіпергеометричного рівняння. Для коефіцієнтів цих розкладів отримано досить прості тричленні рекурентні співвідношення.

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