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LETTER TO THE EDITOR

Non-perturbative uniform wavefunctions of coupled radial Schrödinger equations

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Abstract. A uniform approximation is used with the Green function method to find the total wavefunctions of scattering coupled equations. A simple and analytical expression of non-diagonal terms of the R matrix is derived.

Using the well known uniform approximation (Berry and Mount 1972, Child 1974, Eu 1984), we develop in two steps a method to find uniform solutions of coupled scattering equations. The intent is to provide accurate uniform wavefunctions in a non-perturbative way. Such solutions are obtained in the case of a single equation and the distorted wave coupled equations lead to an interesting analytical expression of the non-diagonal R-matrix elements. These results are used to solve a two-state scattering set of coupled equations without perturbation approximations. Finally we give some areas of applications.

The uniform solution of the homogeneous Schrödinger equation is now well established (Berry and Mount 1972, Eu 1984, Brault 1987):

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}\psi(r)+\frac{p^2(r)}{\hbar^2}\psi(r)=0 \tag{1}$$

with

$$\psi(r)=\hbar^{-2/3}(x(r)/p^2(r))^{1/4}\{\alpha\,\mathrm{Ai}(\hbar^{-2/3}x(r))+\beta\,\mathrm{Bi}(\hbar^{-2/3}x(r))\} \tag{2a}$$

where

$$\begin{aligned} x(r)&=-\left(\frac{3}{2}\int_{r_0}^{r}p(r')\,\mathrm{d}r'\right)^{2/3} \qquad r\geqslant r_0\\ x(r)&=\left(\frac{3}{2}\int_{r_0}^{r}p(r')\,\mathrm{d}r'\right)^{2/3} \qquad r\leqslant r_0. \end{aligned} \tag{2b}$$

$\mathrm{Ai}(x)$ and $\mathrm{Bi}(x)$ are the two linearly independent Airy functions and r_0 is the single turning point. In this case for $x>0$, the $\psi(r)$ must exponentially decrease and thus β must equal zero, while α will be given by normalisation conditions.

Note this approximate wavefunction is a solution to the comparison equation (Berry and Mount 1972):

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}x^2}-\frac{x}{\hbar^2}\right)\psi(x)=0$$

and was successfully used in inelastic and reactive scattering (see Brault *et al* 1987 and references therein). Usually the comparison equation does not invoke $\hbar$ explicitly; it is used here to preserve this dependence.

Consider now the inhomogeneous radial Schrödinger equation

$$\frac{d^2}{dr^2}\psi(r)+\frac{p^2(r)}{\hbar^2}\psi(r)=\frac{1}{\hbar^2}\phi(r) \tag{3}$$

which can be seen as a line of a set of coupled scattering equations.

If we perform the changes of variable and function:

$$x=x(r)$$

$$\psi=z(x)(dx/dr)^{-1/2}$$

equation (3) becomes

$$z''+\left(\frac{1}{\hbar^2}\frac{p^2(r(x))}{(dx/dr)^2}-\frac{1}{2}\frac{1}{(dx/dr)^2}\{x,r\}\right)z=\frac{1}{\hbar^2}\frac{\phi(r(x))}{(dx/dr)^{3/2}}$$

where $\{x, r\}=x'''/x'-\frac{3}{2}(x''/x')^2$ is the Schwartzian derivative. In the semiclassical limit, where $\hbar\to 0$, we shall neglect this term. The solutions (2*a*) are found using the same procedure applied to equation (1).

The uniform approximation is obtained when $p^2(r)(dx/dr)^{-2}=-x$ which leads to

$$x=\left(\frac{3}{2}\int_{r_0}^{r}p(r')\,dr'\right)^{2/3}$$

so that the turning point r_0 leads to $x=0$. Therefore (3) takes the form:

$$z''-\frac{x}{\hbar^2}z=\frac{1}{\hbar^2}\frac{\phi(r(x))}{(dx/dr)^{3/2}}. \tag{4}$$

To find the particular solution of (4) we write the right-hand side as

$$F(x)=F(0)+F(x)-F(0).$$

We now look for the particular solutions of the following two equations:

$$z_1''-\frac{1}{\hbar^2}xz_1=-\frac{1}{\hbar^2}(F(x)-F(0)) \tag{5a}$$

$$z_2''-\frac{1}{\hbar^2}xz_2=-F(0)/\hbar^2. \tag{5b}$$

When $\hbar\to 0$, an approximate solution to (5*a*) is given by (Nayfeh 1973)

$$z_1=(F(x)-F(0))/x. \tag{6}$$

The solution of (5*b*) may be obtained in terms of the solution of the inhomogeneous Airy equation (Lee 1980):

$$y''-xy=-\pi^{-1}\Rightarrow y=\mathrm{Gi}(x) \tag{7}$$

$$y''-xy=+\pi^{-1}\Rightarrow y=\mathrm{Hi}(x). \tag{8}$$

In his book Nayfeh (1973) used the $\mathrm{Hi}(x)$ function. For our scattering point of view we choose $\mathrm{Gi}(x)$ which has good asymptotic behaviour for large internuclear separation (Abramowitz and Stegun 1965).

We can now write the uniform semiclassical solution of (3) as the sum of the expressions (6) and (7), then

$$\psi(r)=\frac{\pi}{\hbar^{2/3}}\frac{\phi(r_0)}{\alpha^{3/2}(r_0)}\left(\frac{x(r)}{p^2(r)}\right)^{1/4}\mathrm{Gi}(\hbar^{-2/3}x(r))-\frac{1}{p^2(r)}\left[\phi(r)-\left(\frac{\mathrm{d}x}{\mathrm{d}r}\right)^{3/2}\frac{\phi(r_0)}{\alpha^{3/2}(r_0)}\right] \tag{9}$$

where

$$\alpha(r_0)=\lim_{r\to r_0}\left(\frac{x(r)}{p^2(r)}\right)^{1/4}=\left(\frac{\mathrm{d}p^2}{\mathrm{d}r}\right)^{-1/3}_{r=r_0}.$$

Finally, as $\hbar\to 0$, the first term of (9) is the dominant one, which gives the uniform solution:

$$\psi(r)=\frac{\pi}{\hbar^{2/3}}\frac{\phi(r_0)}{\alpha^{3/2}(r_0)}\left(\frac{x(r)}{p^2(r)}\right)^{1/4}\mathrm{Gi}(\hbar^{-2/3}x(r)). \tag{10}$$

One can apply this result to the resolution of coupled equations involved in collision theory. Consider the distorted wave coupled radial equations (Child 1974):

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}\psi_1(r)+\frac{p_1^2(r)}{\hbar^2}\psi_1(r)=0 \tag{11a}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}\psi_2(r)+\frac{p_2^2}{\hbar^2}\psi_2(r)=W(r)\psi_1(r). \tag{11b}$$

Using (2*a*) and (2*b*), an approximate solution of (11*a*) is:

$$\psi_1(r)=\hbar^{-2/3}\left(\frac{x_1(r)}{p_1^2(r)}\right)^{1/4}\mathrm{Ai}(\hbar^{-2/3}x_1(r)).$$

Thus with the help of (10), $\psi_2(r)$ becomes

$$\psi_2(r)=\frac{\pi\hbar^{-4/3}}{\alpha_2^{3/2}(r_2)}W(r_2)\left(\frac{x_1(r_2)}{p_1^2(r_2)}\right)^{1/4}\mathrm{Ai}(\hbar^{-2/3}x_1(r_2))\left(\frac{x_2(r)}{p_2^2(r)}\right)^{1/4}\mathrm{Gi}(\hbar^{-2/3}x_2(r))$$

where the labels 1, 2 refer to the channels 1 and 2. r_2 is the turning point in the channel 2. If we recall the definition of the reactance R matrix (Child 1974), with the asymptotic behaviour of $\mathrm{Gi}(x)$, i.e.

$$\psi_2(r)\underset{r\to\infty}{\sim}R_{21}\frac{1}{p_2^{1/2}(r)}\cos\left(\frac{1}{\hbar}\int^r p_2(r')\,\mathrm{d}r'+\frac{\pi}{4}\right).$$

The non-diagonal R-matrix element is readily obtained as

$$R_{21}=\frac{\sqrt{\pi}}{\alpha_2^{3/2}(r_2)}W(r_2)\left(\frac{x_1(r_2)}{p_1^2(r_2)}\right)^{1/4}\mathrm{Ai}(\hbar^{-2/3}x_1(r_2))$$

which can provide the S- or T-matrix elements. It could be interesting to compare this result with the Green function method used by Burnett and Belsley (1983). Indeed the Green function solution of

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{p^2(r)}{\hbar^2}\right)G(r,r')=\frac{\delta(r-r')}{\hbar} \tag{12a}$$

is found to be in the semiclassical limit:

$$G(r,r')=-\pi\hbar^{-4/3}\left(\frac{x(r)}{p^2(r)}\right)^{1/4}\left(\frac{x(r')}{p^2(r')}\right)^{1/4}\begin{cases}\mathrm{Ai}(\hbar^{-2/3}x(r))\mathrm{Bi}(\hbar^{-2/3}x(r')) & r>r'\\ \mathrm{Ai}(\hbar^{-2/3}x(r'))\mathrm{Bi}(\hbar^{-2/3}x(r)) & r<r'.\end{cases} \tag{12b}$$

Therefore the semiclassical solution of (3) is given by:

$$\psi(r) = -\pi\hbar^{-4/3}\left(\frac{x(r)}{p^2(r)}\right)^{1/4}\left[\mathrm{Bi}(\hbar^{-2/3}x(r))\int_0^r \phi(r')\left(\frac{x(r')}{p^2(r')}\right)^{1/4}\mathrm{Ai}(\hbar^{-2/3}x(r'))\,\mathrm{d}r' + \mathrm{Ai}(\hbar^{-2/3}x(r))\int_r^\infty \mathrm{Bi}(\hbar^{-2/3}x(r'))\left(\frac{x(r')}{p^2(r')}\right)^{1/4}\phi(r')\,\mathrm{d}r'\right]. \tag{13}$$

For comparison we can look at the asymptotic behaviour of expressions (10) and (12). From (13) we have:

$$\psi(r) \underset{r\to\infty}{\sim} -\pi\hbar^{-4/3}\left(\frac{x(r)}{p^2(r)}\right)^{1/4}\mathrm{Bi}(\hbar^{-2/3}x(r))\int_0^\infty \phi(r')\left(\frac{x(r')}{p^2(r')}\right)^{1/4}\mathrm{Ai}(\hbar^{-2/3}x(r'))\,\mathrm{d}r'$$

but $\mathrm{Bi}(z)$ has the same asymptotic behaviour as $\mathrm{Gi}(z)$ (Abramowitz and Stegun 1965) and therefore (10) and (13) behave similarly at infinity. For clarity we propose now to solve a two-state scattering problem which can be represented by the following two coupled radial equations:

$$\psi_1''(r) + \frac{1}{\hbar^2}p_1^2(r)\psi_1(r) = W(r, \mathrm{d}/\mathrm{d}r)\psi_2(r) \tag{14a}$$

$$\psi_2''(r) + \frac{1}{\hbar^2}p_2^2(r)\psi_2(r) = W(r, \mathrm{d}/\mathrm{d}r)\psi_1(r) \tag{14b}$$

where $p_i(r)$ are the local momenta, $W(r, \mathrm{d}/\mathrm{d}r)$ is the coupling term (either radial or electronic) and the $\psi_i(r)$ are the radial wavefunctions.

The solutions can be written in terms of the Green functions $G_1(r, r')$ and $G_2(r, r')$:

$$\psi_1(r) = \psi_1^0(r) + \int_0^\infty G_1(r, r')\,W(r')\psi_2(r')\,\mathrm{d}r'$$

$$\psi_2(r) = \psi_2^0(r) + \int_0^\infty G_2(r, r')\,W(r')\psi_1(r')\,\mathrm{d}r'$$

$\psi_i^0(r)$ being the solutions of the uncoupled equations which can be expressed as the wavefunctions ($2a$). If we insert the second equation into the first one, we find

$$\psi_1(r) = \psi_1^0(r) + \int_0^\infty G_1(r, r')\,W(r')\psi_2^0(r')\,\mathrm{d}r' + \int_0^\infty\int_0^\infty G_1(r, r')G_2(r', r'')\,W(r')\,W(r'')\psi_1(r')\,\mathrm{d}r'\,\mathrm{d}r''$$

and $\psi_2(r)$ is obtained by exchanging the labels 1 and 2. Then the set ($14a, b$) is equivalent to the two uncoupled equations:

$$\psi_1(r) = \varphi_1(r) + \int_0^\infty \Phi_{12}(r, r'')\,W(r'')\psi_1(r'')\,\mathrm{d}r'' \tag{15a}$$

$$\psi_2(r) = \varphi_2(r) + \int_0^\infty \Phi_{21}(r, r'')\,W(r'')\psi_2(r'')\,\mathrm{d}r'' \tag{15b}$$

with

$$\varphi_1(r) = \psi_1^0(r) + \int_0^\infty G_1(r, r')\,W(r')\psi_2^0(r')\,\mathrm{d}r'$$

$$\Phi_{12}(r, r'') = \int_0^\infty G_1(r, r')G_2(r', r'')\,W(r')\,\mathrm{d}r'.$$

$\varphi_2(r)$ and $\Phi_{21}(r, r'')$ are obtained putting 1 in place of 2 and conversely. Note that the approximate solution $\psi_i(r) \approx \varphi_i(r)$ is the distorted wave one.

We recall that the Green function $G(r, r')$ is a solution of the equation

$$\frac{d^2 G(r, r')}{dr^2} + \frac{1}{\hbar^2} p^2(r) G(r, r') = \frac{\delta(r - r')}{\hbar}$$

and the inhomogenous solution of

$$F''(r) + \frac{1}{\hbar^2} p^2(r) F(r) = \frac{H(r)}{\hbar^2}$$

is, after expression (10),

$$F(r) = \frac{\pi \hbar^{-2/3}}{\alpha^{3/2}(r_0)} H(r_0) \left(\frac{x(r)}{p^2(r)}\right)^{1/4} \mathrm{Gi}(\hbar^{-2/3} x(r)) \tag{16a}$$

and in terms of the Green function:

$$F(r) = \int_0^\infty G(r, r') H(r')\, dr'. \tag{16b}$$

Then the kernel

$$\Phi_{12}(r, r'') = \int_0^\infty G_2(r', r'')(G_1(r, r') W(r'))\, dr'$$

is a solution of the equation:

$$\left(\frac{d^2}{dr''^2} + \frac{1}{\hbar^2} p^2(r'')\right) \Phi_{12}(r, r'') = G_1(r, r'') W(r'')$$

for which the semiclassical solution, using the identity between (16*a*) and (16*b*), is

$$\Phi_{12}(r, r'') = \frac{\pi \hbar^{-2/3}}{\alpha_2^{3/2}(r_2)} G_1(r, r_2) W(r_2) \left(\frac{x_2(r'')}{p_2^2(r'')}\right)^{1/4} \mathrm{Gi}(\hbar^{-2/3} x_2(r''))$$

where r_i is the turning point for each channel; then the integral term in (15*a*) takes the form:

$$\int_0^\infty \Phi_{12}(r, r'') W(r'') \psi_1(r'')\, dr''$$

$$= \frac{\pi \hbar^{-2/3}}{\alpha_2^{3/2}(r_2)} W(r_2) G_1(r, r_2) \int_0^\infty \left(\frac{x_2(r'')}{p_2^2(r'')}\right)^{1/4} W(r'') \mathrm{Gi}(\hbar^{-2/3} x_2(r'')) \psi_1(r'')\, dr''. \tag{17}$$

On the other hand, following (16*a*, *b*), the term $\int_0^\infty G_1(r, r') W(r') \psi_2^0(r')\, dr'$ is given by its semiclassical form:

$$\varphi_1(r) = \psi_1^0(r) + \frac{\pi \hbar^{-2/3}}{\alpha_1^{3/2}(r_1)} W(r_1) \psi_2^0(r_1) \left(\frac{x_1(r)}{p_1^2(r)}\right)^{1/4} \mathrm{Gi}(\hbar^{-2/3} x_1(r)). \tag{18}$$

Thus we can express the solution $\psi_1(r)$ as the integral equation:

$$\psi_1(r) = \varphi_1(r) + G_1(r, r_2) \int_0^\infty F(r'') \psi_1(r'')\, dr'' \tag{19}$$

with

$$F(r'')=\frac{\pi\hbar^{-2/3}}{\alpha_2^{3/2}(r_2)}W(r_2)\left(\frac{x_2(r'')}{p_2^2(r'')}\right)^{1/4}W(r'')\mathrm{Gi}(\hbar^{-2/3}x_2(r'')).$$

Let

$$\lambda=\int_0^\infty F(r'')\psi_1(r'')\,\mathrm{d}r''$$

then

$$\psi_1(r)=\varphi_1(r)+\lambda G_1(r,r_2)$$

and, putting this quantity in (19), we find:

$$\lambda=\left(\int_0^\infty F(r'')\varphi_1(r'')\,\mathrm{d}r''\right)\left(1-\int_0^\infty F(r'')G_1(r'',r_2)\,\mathrm{d}r''\right)^{-1}. \tag{20}$$

The integral

$$\int_0^\infty F(r'')G_1(r'',r_2)\,\mathrm{d}r''$$

can be evaluated in the same way as before to give:

$$\int_0^\infty G_1(r'',r_2)F(r'')\,\mathrm{d}r''$$
$$=\frac{\pi^2}{\hbar^{4/3}}\frac{W(r_1)W(r_2)}{(\alpha_1(r_1)\alpha_2(r_2))^{3/2}}\left(\frac{x_1(r_2)x_2(r_1)}{p_1^2(r_2)p_2^2(r_1)}\right)^{1/4}\mathrm{Gi}(\hbar^{-2/3}x_1(r_2))\mathrm{Gi}(\hbar^{-2/3}x_2(r_1)). \tag{21}$$

The integral

$$\int_0^\infty F(r'')\varphi_1(r'')\,\mathrm{d}r''$$

could be calculated either by a numerical quadrature or by a stationary phase method. Then using results (19) and (20) we find the semiclassical wavefunction

$$\psi_1(r)=\varphi_1(r)+\left(G_1(r,r_2)\int_0^\infty F(r'')\varphi_1(r'')\,\mathrm{d}r''\right)\left(1-\int_0^\infty F(r'')G_1(r'',r_2)\,\mathrm{d}r''\right)^{-1}. \tag{22}$$

$G_1(r, r_2)$ is given by the appropriate expression (12*b*) stated by Burnett and Belsley (1983). The values for which the denominator becomes zero correspond to the bound states of the system.

The wavefunctions given by formulae (10) and (22) are the main results we propose in this paper. The first one was used to infer a simple analytical *R*-matrix element in the distorted wave approximation frame.

The knowledge of complete inelastic scattering uniform wavefunctions (22) is of great interest in laser-assisted collision phenomena. They are in particular very useful for calculating the Franck-Condon factors which take the form $|\langle\psi_1|D|\psi_2\rangle|^2$ where D is the electric dipolar operator. With such uniform wavefunctions, the collision is treated accurately even in the collisional interaction region. In a forthcoming paper we intend to apply these results to reactive scattering.

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