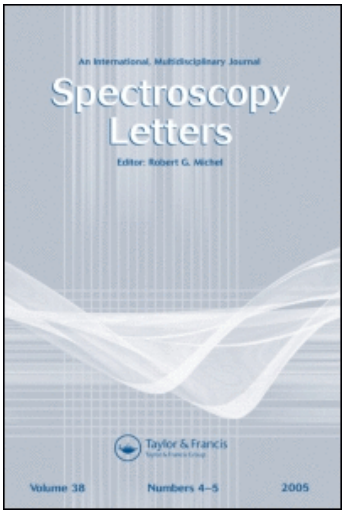

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The Quantum and Semiclassical Phase Formalism for Obtaining the 1D Eigenfunctions

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THE QUANTUM AND SEMICLASSICAL PHASE FORMALISM FOR OBTAINING THE 1D EIGENFUNCTIONS

Key words: Radial Schrodinger equation, semiclassical approximation, vibrotional wavefunction.

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Abstract.

The quantum phase formalism, suggested earlier (Abarenov A.V. and Stolyarov A.V. J.Phys.B, (1990) 23 2419-26), for the solution of the one-dimensional (1D) eigenvalue problem, is applied for eigenfunctions and its overlap integrals . The quantum phase and amplitude functions of the offered method is found to concide with semiclassical ones under standart semiclassical conditions ($p' \ll p$). It made possible to obtain the closed form of wavefunctions and energies, which is equivalent to those of $\hbar^2$ order W.K.B. expansion. The method is the most efficient for strongly oscillating eigenfunctions, i.e. in the high-energy limit.

1. Introduction.

Much effort has been devoted to searching for the most efficient and convinient methods of solution of one-dimensional (1D) eigenvalue problem. However, one can not usually take the advantages of these methods for solving eigenfunction problem straight off. Moreover, the majority of these ones have significant drawback — their accuracy is rapidly decreased for the highly oscillatory eigenfunctions, i.e. as the vibrational quantum number v for bound states and energy E for continuum states increases.

The well-known direct step-by-step numerical integration (so-called "shooting") method is widely used for both eigenvalues, as eigenfunctions of 1D Schrodinger equation . Obviously, its accuracy is defined by the particular numerical scheme applied for integration. The ordinary or renormalized Numerov [1] algorithm is often employed to integrate the 1D Schrodinger equation, since this procedure is efficient, accurate and numerically stability for both one-minimum and double-minimum molecular potentials [2].

It is easy to show that for Numerov algorithm the relative error η of wavefunction inside the classically allowed region at high v grows as a third power level energy E [3]. Moreover, the value η grows as $E^{n/2+1}$ inside the classicaly allowed regions in any finite-difference scheme of order n. This dependence seems to be not appropriate for states with highly oscillatory eigenfunctions.

To overcome this problem, we apply the phase formalism, suggested earlier for searching eigenvalues [4], to direct numerical integration 1D Schrodinger equation.

2. Modified phase method for 1D eigenfunctions and its semiclassical limit.

Let us rewrite the 1D Schrodinger equation using a new variables

$$y = g \sin(\varphi) \tag{1a}$$

$$y' = a\, g \cos(\varphi), \tag{1b}$$

where a - is some function and prime indicates the first-order diffe-

rention in radial coordinate r. So we obtain differential equations for phase φ and amplitude g :

$$\varphi' = a\text{-}\sin\left\{\{a\text{-}(E\text{-}U)/a\}\sin(\varphi)\text{-}\{a'/a\}\cos(\varphi)\right\} \quad (2a)$$

$$g'/g = \cos\left\{\{a\text{-}(E\text{-}U)/a\}\sin(\varphi)\text{-}\{a'/a\}\cos(\varphi)\right\}, \quad (2b)$$

where both energy E and potential U(r) are expressed in Aston unit. Now, a(r) is supposed to be equal to classical momentum p(r) in the classical accessiable region: $a=p(r)=\sqrt{E-U(r)}$. Then, eqs.(2) for phase φ_p and amplitude g_p take the following form:

$$\varphi_p' = p + (p'/2p)\ \sin(2\varphi_p) \quad (3a)$$

$$g_p'/g_p = -(p'/2p)(\ 1+\cos(2\varphi_p)\ ) \quad (3b)$$

Further, upon the substitution $\varphi_p \equiv \varphi_{sc} + \alpha_p$ and $g_p = g_{sc}e^{-\beta_p}$, where $\varphi_{sc}=\int pdr+\varphi_o$ and $g_{sc}=C/\sqrt{p}$ are first-order semiclassical phase and amplitude, respectively [5], we arrive the following equations for the quantum correction functions α_p and β_p:

$$\alpha_p' = (p'/2p)\ \sin(2\varphi_p) \quad (4a)$$

$$\beta_p' = (p'/2p)\ \cos(2\varphi_p) \quad (4b)$$

So the total wavefunction y is:

$$y = C/\sqrt{p}\ e^{-\beta_p}\ \sin\left\{\int pdr + \alpha_p + \varphi_o\right\} \quad (5)$$

As it is appears from eq.(4),the amplitudes of the α_p and β_p functions falls down rapidly in the classical allowed region under condition $p' \ll p$. Therefore,the moduluses of the α_p and $\beta_p \Rightarrow 0$ and the eq.(5) is transformed into well-known first-order W.K.B. expression of wavefunction.

To establish this correspondence to second-order, it is useful to rewrite eq.(4a) using relation (1a). Thus,

$$\alpha_p' = (p'/2p^2g^2)\ (y^2)' \quad (6)$$

and, finally,

$$\alpha_p' = (p'g'/2p^2g)\ \sin^2(\varphi_p) + (p'/2p^2)\ \{\sin^2(\varphi_p)\}' \quad (7)$$

If the conditions

$$g_p' \approx g_{sc}' \ll \sin'(\varphi_p) \quad (8)$$

are true, we immediately obtain the approximate expression for α_p:

$$\alpha_p \approx (p'/2p^2)\ \sin^2(\varphi_p) - \int (p')^2/4p^3 dr, \quad (9)$$

which is closed to conventional W.K.B. expansion of the eigenfunction to terms of $\hbar^2$ order.

From a physical point of view the supposition (8) corresponds to the motion of highly excited particle in the slowly varying potential. Quantitutively, this means that $U' \ll 4p^3$, what is exactly equivalented to well-known condition of the validity of the semiclassical approximation.

Eq.(9) justifies the assumption about the best choice matching points for trial phase functions near the potential minimum [4]. In this case $p'(R_c) \approx 0$ and the first term in eq.(9) vanishes. Therefore, the smoothness of total phase function $\varphi_t(R_c,E)$ from trial energy E reaches a maximum.

Using the quantization rule for total quantum phase function, i.e. $\varphi_t(R_c,E)=\pi(v+1)$, the semiclassical second-order quantization rule [6] could be derive from eq.(9):

$$\int_{r_1}^{r_2} p\,dr = \pi(v+1) + \int_{r_1}^{r_2} (p')^2/4p^3\,dr \qquad (10)$$

Obviously, eqs.(4) are not valid in the vicinity of the turning points ($p \approx 0$) and in the classically inaccessible regions. As the same time, the conventional phase methods [7], which are based on the substitution: $y'/y=tg(\varphi)$ (i.e. a=1 in our notations), are correct for all integration regions. However, in this case the phase functions φ_1 is found to have ladder-like form in the classical allowed region , and their applications is apperently not so efficient.

In this end, the reasonable compromise between the two substitutions a=1 and a=p(r) are seemed to consist in the choice $a=p(r_m)=p_m=\text{const}$, where r_m corresponds to potential minimum. Then $a'=0$ and, introducing the difference between φ_m and φ_{sc} as $\varphi_m = \varphi_{sc} + \alpha_m$ again, we obtain equations for α_m and g_m functions:

$$\alpha_m' = \{p_m - p\}\{\cos^2(\varphi_m) - (p/p_m)\sin^2(\varphi_m)\} \qquad (11a)$$

$$g_m'/g_m = ((p_m^2 - p^2)/2p_m)\sin(2\varphi_m) \qquad (11b)$$

Further, recalling that $a=p(r_m)=\sqrt{E_m}$, where energy E_m is calculataed from the potential minimum ($U(r_m)=0$). and introducing the new difference function $\alpha_m = \sqrt{E_m}r - \varphi_m$, which can be considered as the correction to free particle motion, one obtains the simpler expressions for α_m and g_m:

$$\alpha'_m = (U/2\sqrt{E_m})\ \sin^2(\varphi_m) \qquad (12a)$$

$$g'_m/g_m = (U/2\sqrt{E_m})\sin(2\varphi_m) \qquad (12b)$$

Note, that eqs.(11) and (12) in contrast to eqs.(3) and (4) are not required the knowledge of the first derivative of momentum.

From eqs.(11) and (12) it is easy verify, that the amplitudes of α_m and g_m functions decreases monotonically as moving toward into the classical allowed region, although more slowly than those of α_m and g_m obtained by replacment a=p(r). Therefore, the function α_m vanishes in classical allowed region and the corresponding total wavefunction y becomes close to its semiclasssical analogues. At the same time, eqs.(11) and (12) hold true in the classical forbidden regions and near the turning points.

In additional,the phase methods can be applied to estimate the overlap integrals from the product of highly oscillating wavefunctions, numerically. Obviously, the application any finite-difference scheme is resulted to the pointwise representation of total wavefunctions, which is extremely unefficient here. Quite the reverse,the use of the quasianalitical form of y (eq.(5)) permits to present this integrals as $\int V\ g_1 g_2 \cos(\varphi_1-\varphi_2)dr$, where we neglect of strongly oscillating term $\cos(\varphi_1+\varphi_2)$. Therefore,it is possible to reduce a number of oscillations of the integrand function, especially when phase values of both wavefunctions are closed to each other, i.e. $\varphi_1 \approx \varphi_2$.

Moreover, the evaluation of Franck-Condon type integrals may be further simplified in the framework of the saddle-point method,which is applied for calculation the semiclassical matrix elements [8]. For this porpose it is appropriate to represent the total wavefunction in the form (5). In this case, transcendent equation for saddle point r^* searching takes the following form

$$p_2 - p_1 = (p'_1/2p_1)\sin(2\varphi_1) - (p'_2/2p_2)\sin(2\varphi_2) \qquad (13)$$

and the difference of stationary local phases Φ equal to $\Delta\varphi_{sc}(r^*) + \Delta\alpha(r^*)$. Using eq.(9), it is easy to found the ralative errors of matrix elements, estimated with the semiclassical wavefunctions -- $\eta_{sc} \sim p'/p$ and the shift in the location saddle point — $\Delta r^* \sim 1/p$.

3.Conclusions.

It is readily seen,that the relative errors of total wavefunctions y inside the classical allowed regions are proportional to p'/p and $U/\sqrt{E_m}$, when the eqs.(4) or (12) are applied to obtain eigenfunctions, respectively. It allowes one to discuss those methods are the most suitable and natural schemes for the direct integration 1D Schrodinger equation in the regions satisfied with following conditions $p' \ll p$ and/or $U \ll E$. In general, these conditions are met in the high-energy limit,i.e. near and above the dissociation threshould for both bound and continuum states. Note, that the corresponding total wavefunctions are highly oscillatory nature, so the conventional finite-difference schemes are failed.

On the other hand,these methods are unefficient with compared to finite-difference ones in the classical forbidden regions and near the turning points. Obviously,it is possible to combine this two methods at any point of internuclear distance by using the relationship between the phase function and the logderivative of total wavefunction -- $\varphi=n\pi+\mathrm{arctg}\{ay/y'\}$.

The introduced correction functions α and β can be employed to control the accuracy of wavefunctions obtained under different semiclassical approachs.

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