

Improved calculations of the sensitivity density between phase shift and potential energy function

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Abstract: Retrieving the potential energy function at the quantum level, based on experimental data of thermophysical properties, such as the quantum second virial coefficient and the quantum viscosity coefficients, requires the sensitivity density of the phase shift with respect to the potential energy function $\delta\eta_l(k)/\delta V(r)$ [1]. The calculation of this quantity, because the large integration limits, necessary to find the asymptotic solution of the Schrödinger radial equation with the correct amplitude, has been performed with the approximate Langer JWKB method [1]. In 2014 [2] we showed how the quantity $\delta\eta_l(k)/\delta V(r)$ could be found by means of a system of coupled differential equations involving the Calogero's equation. This theory was recently used to recover the potential energy function for ^4He from quantum viscosity coefficient data from 1 to 5 K [3]. In the present work it is shown how this approach can be reformulated to a new integral representation. The Calogero's equation in terms of the Ricatti-Bessel functions j_l and y_l for the reduced potential $U(\rho)$ is $\frac{d\eta_l(\rho;k)}{d\rho} = -\frac{U(\rho)}{k} \{j_l(k;\rho) \cos[\eta_l(\rho;k)] - y_l(k;\rho) \sin[\eta_l(\rho;k)]\}^2$. By the derivation of this equation with respect to the potential at a specific r coordinate, that is $\frac{\partial}{\partial V(r)} \frac{d\eta_l(\rho;k)}{d\rho} = \frac{d}{d\rho} \frac{\partial\eta_l(\rho;k)}{\partial V(r)} \equiv \frac{dS_l(\rho;k)}{d\rho}$ one obtains the differential equation, which solved up to the asymptotic limit of $\rho \rightarrow \infty$, provides the sensitivity $S_l(k, r) = (\delta\eta_l(k)/\delta V(r))\Delta\rho$. This equation must be solved coupled to $G(\rho; r) \equiv \partial U(\rho)/\partial V(r)$, which has the value of $2\mu/\hbar^2$ if $\rho = r$ or 0 if $\rho \neq r$. Since $G(\rho; r)$ has finite value only at r , the sensitivity begins to be accumulated only from that point, then we suggest to transform the problem into the initial value problem (PVI) below,

$$\frac{dS_l(\rho; k, r)}{d\rho} = \frac{U(\rho)}{k} \{2j_l(k\rho)y_l(k\rho) \cos[2\eta_l(\rho; k)] + [j_l^2(k\rho) - y_l^2(k\rho)] \sin[2\eta_l(\rho; k)]\} S_l(\rho; k, r) \quad (1)$$

$$S_l^0(r; k) = -\frac{2\mu}{k\hbar^2} \{j_l(kr) \cos[\eta_l(r; k)] - y_l(kr) \sin[\eta_l(r; k)]\}^2 \Delta r. \quad (2)$$

Integration can now be performed from r . The above PVI can still be simplified, given that $\frac{\partial\eta_l(k)}{\partial V(r)} = \frac{\delta\eta_l(k)}{\delta V(r)}\Delta\rho$, the convenient integral representation is obtained,

$$\frac{\delta\eta_l(k)}{\delta V(r)} = S_l^0(r; k) e^{\int_r^\infty f_l(\rho; k) d\rho}, \quad (3)$$

in which,

$$f_l(\rho; k) = \frac{U(\rho)}{k} \{2j_l(k\rho)y_l(k\rho) \cos[2\eta_l(\rho; k)] + [j_l^2(k\rho) - y_l^2(k\rho)] \sin[2\eta_l(\rho; k)]\}, \quad (4)$$

and $\Delta r = 1$ in $S_l^0(r; k)$. In equation (3) the integrand depends only on $\eta_l(\rho; k)$, therefore, solving the Calogero's equation only once, for a given k and l , can be find the sensitivity density $\delta\eta_l(k)/\delta V(r)$ for several coordinates, unlike the previous method [2], in which the Calogero's equation should be solved several times coupled, and in ranges where the sensitivity was not accumulated. Figure 1 (a) shows $\delta\eta_l(k)/\delta V(r)$ calculated by equation (3) and with the Langer JWKB approximation using the potential of the reference [4] for the helium system. The radial wave function $u_l(r; k)$, calculated by the relation $\delta\eta_l(k)/\delta V(r) = -(\mu/\hbar^2)u_l^2(r; k)$, is also presented (Figure 1 (b)).

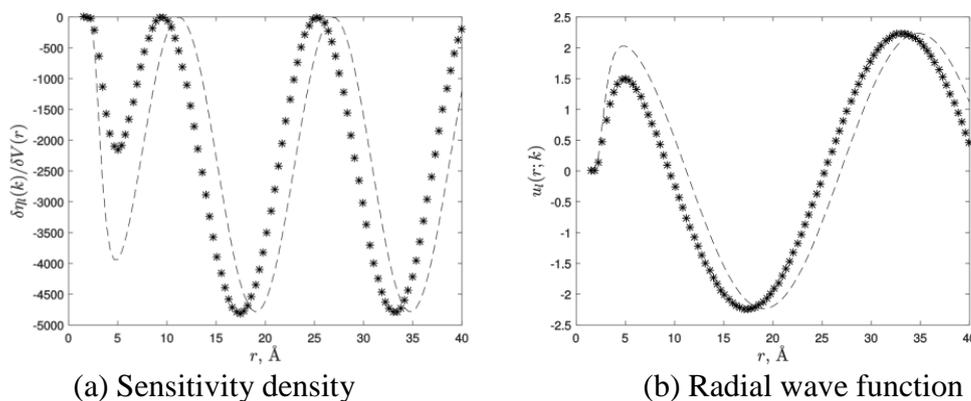


Figure 1: Numeric results at $l = 0$ and $k = 0.2 \text{ \AA}^{-1}$: obtained from equation (3) (dashed line); obtained in the Langer JWKB approximation (stars).

Figure 1 (a) highlights the error when using the Langer JWKB approximation, occurring a deviation at the position of the minima and at its intensities. The largest deviation occurs near 5 \AA , region of interest for the inversion of potential energy function. The presented method (Equation 3) is precise and simple for computational implementation, which can be used to recover the potential energy function in sensitivity analysis approach, from thermophysical properties within the quantum treatment.

Key-words: Calogero's equation, phase shift, sensitivity analysis approach, sensitivity density, potential energy function.

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