Accurate potential energy curve for helium dimer retrieved from viscosity coefficient data at very low temperatures

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Abstract

The long range potential of helium-helium interaction, which requires accurate \textit{ab initio} calculation, due to the small value of the potential depth, approximately 11 K \((9.5 \times 10^{-4} \text{ eV} = 0.091 \text{ kJ/mol})\) at 2.96 Å, will be obtained in this study by an alternative technique. This work presents a robust and consistent procedure that provides the long range potential directly from experimental data. However, it is difficult to obtain experimental data containing information regarding such a small potential depth. Thereby, sensitivity analysis will be used to circumvent this difficulty, from which viscosity data at lower temperatures \((< 5 \text{ K})\) were chosen as appropriate data to be used to retrieve the potential function between 3 and 4 Å. The linear relationship between the potential energy function and the viscosity coefficient will be established under quantum assumptions and the Bose-Einstein statistic. The use of quantum theory is essential, since the temperatures are below 5 K. The potential obtained in this study describes the viscosity with an average error of 1.68 % that is less than the experimental error (5 %), with the results being similar to those obtained for recent \textit{ab initio} potentials.

\textbf{Keywords:} Variable phase method. Viscosity coefficient. Low temperature. Sensitivity analysis.
1 Introduction

Potential energy functions play a central role in chemistry, and from these functions, the properties of a system can, in principle, be determined. Often, the potential energy function is obtained from \textit{ab initio} methods, but it can also be determined from experimental data using inverse techniques. Inverse problems theory to handle experimental data has been applied to refine potential energy functions from the second virial coefficient,[1, 2] differential cross-sections[3, 4] and phase shifts.[5]

The helium diatomic system at low temperatures has received considerable attention in recent years due to quantum and relativistic effects in their thermodynamics and transport properties.[6] The theoretical interpretation of the results has been performed with the \textit{ab initio} potential function.[7] The helium dimer has a very small potential well depth, measuring approximately 11 K,[8, 9] consequently, highly accurate calculations are required to obtain the potential energy function.[8, 9]

The present paper presents an alternative way to refine the helium potential energy function from viscosity coefficient data at low temperatures. Few studies have been conducted along this line and often at high temperatures,[10] limit in which classical theory is valid, and in parametric form, usually for a Lennard-Jones potential energy curve.[11]

To gain insight into this problem, an investigation into the sensitivity[2, 3] of the viscosity coefficient to the potential energy function is conducted, and an adequate temperature range for experimental data was observed. The present study shows a higher sensitivity for long range potential in the temperature range below 5 K. Since it is necessary to use viscosity coefficient data at low temperatures in an inverse procedure, a quantum strategy to refine the potential energy curve is necessary and will be presented in this study.

The inverse problem was divided into two parts: in the first part, the cross-section is obtained from the viscosity coefficient, whereas in the second part, the potential energy function is determined from the cross-section. The solution to the first part was determined using the Tikhonov regularization under a Laplace integral equation formulation. In the second part, the relationship between the potential energy and the total cross-section, which is nonlinear, was linearized by a sensitivity analysis algorithm.[2]

The cross-section sensitivity matrix established has an approximate linear relation between the potential energy and total cross-section. In a previous study,[5] the functional derivative of the quantum phase shift with respect to the potential energy function was established and coupled with the variable phase equation. For the first time, this set of coupled differential
equations was used to establish the cross-section sensitivity matrix within exact quantum theory. This problem is ill-posed, since sensitivity matrix elements possess values that are close to zero. In an attempt to circumvent this problem in a tractable way, the Tikhonov regularization procedure was used again.

The result obtained by the inverse technique was compared with recent ab initio potentials[8, 12] and exhibited excellent agreement. The present work presents a general strategy to obtain an accurate inverted potential, comparable in quality with high level potential energy models and calculations.

2 Theoretical background

General formalism of the direct problem

Chapman-Enskog theory[13, 14] provides a well-established perturbation method to calculate the viscosity coefficient \( \eta \) of a non-ideal gas from the collision integral \( \Omega^{(2,2)} \). In a first order approach, the viscosity coefficient is given by

\[
\eta(T) = \frac{5(\pi m k_B T)^{1/2}}{16\pi \Omega^{(2,2)}}
\]

in which \( m \) is the mass of the system, and \( k_B \) is Boltzmann’s constant. The collision integral of interest to determine the viscosity coefficient is set in the form

\[
\Omega^{(2,2)}(T) = \frac{1}{4\pi (k_B T)^3} \int_0^\infty \exp(-E/k_B T) E^3 Q^{(2)} dE
\]

with \( T \) the temperature and \( E \) the collision energy.

The transport cross-section \( Q^{(2)} \) in classical statistical mechanics is directly related to the scattering angle, but in quantum assumptions and for the Bose-Einstein statistic, the cross-section is associated with the phase shift, as follows:

\[
Q^{(2)}(\kappa) = \frac{8\pi}{\kappa^2} \sum_{l=0,2,4,...} \frac{(l + 1)(l + 2)}{(2l + 3)} \sin^2[\delta_{l+2}(\kappa) - \delta_l(\kappa)]
\]

with \( \kappa = 2\pi \sqrt{2mE/h} \) the wave number, \( h \) Planck’s constant and \( l \) the angular moment. The phase shift \( \delta_l \) is obtained from Calogero’s equation,

\[
\frac{d\delta_l(R; \kappa)}{dR} = -\frac{1}{\kappa} U_{\text{eff}}(R) \sin^2[\kappa R + \delta_l(R; \kappa)]
\]

when \( R \to \infty \), in which \( U_{\text{eff}}(R) = \frac{8\pi^2 \mu}{\hbar^2} E_p(R) + \frac{\mu l(l+1)}{\hbar^2} \) and \( R \) is the interatomic distance and \( \mu \) is the system reduced mass. More details about the Calogero equation can be found in
the published works of Lemes et al.,[5] Viterbo2014 et al.,[15] and Braga and Murrell.[16] The viscosity coefficient as a function of the temperature is determined by solving these equations, obeying the sequence (4), (3), (2) and (1).

The inverse problem strategy

In another approach, it is desired to obtain the potential energy function from the viscosity coefficient in the opposite direction of the direct problem, that is, in the sequence (1), (2), (3) and (4). The first step consists of computing the collision integral $\Omega^{(2,2)}$ from viscosity coefficient data using equation (1) through simple algebraic manipulation. The second step consists of the evaluation of the transport cross-section $Q^{(2)}$ from the collision integral $\Omega^{(2,2)}$, and these quantities are related by equation (2). The bold style was used to represent functions in matrix form. Using the trapezoidal quadrature, equation (2) is transformed to an algebraic form $\Omega^{(2,2)} = KQ^{(2)}$, the solution of which is determined by the Tikhonov regularization method as

$$Q^{(2)} = (K^T K + \lambda I)^{-1} (K^T \Omega^{(2,2)} + \lambda Q_0^{(2)}),$$

in which $Q_0^{(2)}$ is a first approximation for $Q^{(2)}$. With $Q^{(2)}$ found, it is possible to obtain the potential energy $E_p(R)$ from the cross-section through equations (3) and (4).

The main difficulty of this strategy is to obtain the $E_p(R)$ value from $Q^{(2)}(\kappa)$, due to the nonlinear relationship between these two quantities. This difficulty can be avoided by linearization of the problem as follows:

$$\Delta Q^{(2)} = S_Q^* \Delta E_p$$

in which the matrix $S_Q^*$ is the sensitivity matrix, with elements $S_Q^*(\kappa, R^*) = \frac{\partial Q^{(2)}(\kappa)}{\partial E_p(R^*)}$. Nevertheless, it is more appropriate to use equation (6) as

$$\Delta \ln Q^{(2)} = S_Q \Delta \ln E_p$$

with elements of $S_Q$ in a normalized form, such as $S_Q(\kappa, R^*) = S_Q^*(\kappa, R^*) \frac{E_p(R^*)}{Q^{(2)}(\kappa)}$. Here, the adequate solution can not be found by an orthodox inverse matrix algorithm, because the matrix $S_Q$ is ill conditioned. The inverse matrix will be given again by another Tikhonov regularization

$$S_Q^{-1} = (S_Q^T S_Q + \lambda I)^{-1} S_Q^T$$

in which $\lambda$ is a parameter of regularization and is the identity matrix. Finally, the desired solution is given by

$$E_p^{(1)} = E_p^{(0)} (1 + (S_Q^T S_Q + \lambda I)^{-1} S_Q^T \Delta \ln Q^{(2)})$$
in which $E_p^{(0)}$ is an initial guess for $E_p$. In this case, the regularization parameter is chosen by an L-curve, and provides an equilibrium between a residual norm and a solution norm.

The alternative sensitivity matrix calculation

The success of the present method relies on identifying a way to determine the sensitivity matrix. In a previous work,[5] a differential equation for the functional derivative of the quantum phase shift with respect to the potential energy function, $S_{\delta_l}(k, R^*) = \frac{\partial \delta_l(k)}{\partial V(R^*)}$, is established and coupled to Calogero’s equation (4),

$$\frac{d\delta_l}{dR} = -\frac{U_{\text{eff}}(R)}{\kappa} \sin^2(\kappa R + \delta_l)$$

$$\frac{dS_{\delta_l}}{dR} = -\frac{1}{\kappa} [G(R, R^*) \sin^2(\kappa R + \delta_l) + 2U_{\text{eff}}(R) \sin(\kappa R + \delta_l) \cos(\kappa R + \delta_l) S_{\delta_l}]$$

in which $G(R, R^*)$ is given by

$$G(R, R^*) = \frac{\partial U_{\text{eff}}(R)}{\partial E_p(R^*)} = \begin{cases} \frac{8\pi^2 \mu}{\kappa^2}, & R = R^* \\ 0, & R \neq R^* \end{cases}$$

Therefore, the value of $S_{\delta_l}$ at fixed values of $\kappa$ and $R^*$, can be determined from coupled equations (10), at $R \to \infty$ for different angular moments. More details about this approach are given in the work of Lemes et al.[5]

By deriving equation (3) with respect to the potential energy function at $R^*$, the sensitivity cross-section $S'_{Q}(k, R^*)$ will be given by

$$S_{Q}'(\kappa, R^*) = \frac{8\pi}{\kappa^2} \sum_{l=0,2,4,...}^{\infty} \frac{(l+1)(l+2)}{(2l+3)} \sin[2(\delta_{l+2}(\kappa) - \delta_l(\kappa))] \times \left[ S_{\delta_{l+2}}(\kappa, R^*) - S_{\delta_l}(\kappa, R^*) \right]$$

where all of the necessary information is available from the previous step. This method provides a new, simple and exact way to establish the sensitivity cross-section matrix $S_{Q}$ english in equation (9).

Finally, the sensitivity matrix for the viscosity coefficient can be obtained by

$$S_{\eta}(T, R^*) = -\frac{5(\pi m k_B T)^{1/2}}{16\pi} \frac{1}{\Omega^{(2,2)}} S_{\Omega}$$

in which

$$S_{\Omega}(T, R^*) = \frac{1}{4\pi (k_B T)^4} \int_{0}^{\infty} \exp(-E/k_B T) E^3 S'_{Q}(E, R^*) dE.$$
\[ \Delta \eta = S_\eta \Delta E_p \] instead of equation (6). Nevertheless, preliminary studies show that the condition number of matrix \( S_\eta \) is larger than the condition number of matrix \( S_Q \), making this method more difficult than the procedure proposed in this study.

## 3 Results and discussion

### Sensitivity analysis and experimental data

Figure 1(a) shows the contour lines of the normalized sensitivity matrix to the transport cross-section data, \( S_Q \). This result provides important insight into the inverse procedure, such as the choice of the experimental data range to be used.

![Figure 1](image)

From Figure 1(a), it can be observed that the transport cross-section with \( \kappa \) between 0.2 and 0.5 Å\(^{-1}\) has a larger value of sensitivity at interatomic distances between 3 and 4 Å. This region of \( \kappa \) provides experimental data that are more adequate to obtain the long range potential between 3 and 4 Å because small changes in the potential can cause large changes in the transport cross-section. Since the \( \kappa \) values of approximately 0.1 Å\(^{-1}\) correspond to energy values of approximately 0.1 K, it is better to use viscosity experimental data obtained at low temperatures for the inverse procedure. This conclusion can also be obtained from Figure 1(b), showing the sensitivity level curves for viscosity data.

Only a small number of papers have reported experimental data on viscosity coefficients at low temperatures. For the temperature range required to refine the potential curve between 3 and 4 Å, that is, below 5 K, the reference of Becker et al.[17] presents 11 values. However, the quality of these data has been questioned[18] due to the use of an old reference value for equipment calibration, resulting in a positive deviation of approximately 5 % as estimated by Bich and Vogel.[18]

To generate the necessary data of viscosity coefficients, the equation

\[
\frac{\eta}{\text{Pa.s}} = 2.113 \times 10^{-7} \left( \frac{T}{\text{K}} \right)^{1.1} \left\{ 1 + 1.16 \exp \left[ -2.44 \left( \log \left( \frac{T}{\text{K}} \right) + 0.56 \right)^2 \right] \right\},
\]

was used.[19] From this equation, 41 viscosity values, between 1 and 5 K, were determined and used to refine the potential curve. The values adjusted by the equation (15), shown in Figure 2, agreed with the calculated results with the most precise potential for description of the system,[9, 6] with an average error of 0.8735 %, an error lower than that reported for the
experimental data (5 %). Therefore, henceforth we will refer to equation (15) as experimental data.

Figure 2

Recent potentials and initial information

In our inversion procedure, an initial potential curve, $E_p^{(0)}$, is given as \textit{a priori} information. This approximate potential curve is given by

$$
E_p^{(0)}(R) = \begin{cases} 
E_p(R), & R \leq R_1 \\
E_p(R) \times \left\{1 + \varepsilon \left[1 - \cos^2\left[\frac{\pi (R-R_1)}{R_2-R_1}\right]\right]\right\}, & R_1 < R < R_2 \\
E_p(R), & R \geq R_2 
\end{cases}
$$

(16)
as suggested in the reference of Keil and Danielson,\cite{20} in which $R_1 = 2.4$, $R_2 = 4.5$, and $\varepsilon = 0.2$ were used to modify the potential curve $E_p(R)$ between 3 and 4 Å. The function $E_p(R)$ is the \textit{ab initio} potential curve proposed in 2010,\cite{8} henceforth considered to be the reference potential. The $E_p(R)$ curve was previously tested to evaluate the second virial coefficient between 3 and 100 K with excellent agreement with the experimental data.\cite{7} When this potential is compared with the most accurate potential describing the system,\cite{9} the difference is less than 22.4 $\mu$eV, between 2.4 and 4.5 Å. Nevertheless, both curves, Varandas\cite{8} and Przybytek et al.\cite{9}, describe the viscosity coefficient with an error less than 5 % for temperatures between 1 and 5 K. Therefore, both \textit{ab initio} potential curves, namely, those of Varandas\cite{8} and Przybytek et al.\cite{9}, are equally suitable to describe the viscosity coefficient between 1 and 5 K.

The difference between the potential curves $E_p^{(0)}$ and $E_p$ is controlled by the parameter $\varepsilon$, when $\varepsilon$ is equal to 0.2 the average difference is approximately 10 %. In this case, if the potential curve $E_p^{(0)}$ is used to calculate the viscosity data the average error found was 12.46 %, which is greater than the experimental error of 5 %. Therefore, the calculated viscosity data from the potential curve $E_p^{(0)}$ are not within the experimental error, and it is not suitable for estimating the viscosity coefficient.

The determination of the viscosity coefficient from a potential energy curve involves three steps: the determination of the phase shift using equation (4); followed by the determination of the transport cross-section using equation (3); and finally the determination of the collision integral using equation (2) from which the viscosity can be readily calculated. Numerical integration of Calogero’s equation (4) was performed using the Euler algorithm, with a step of $10^{-2}$ Å between 1.5 and 70000 Å. Next, in equation (3), the sum is carried over even
angular moments between 0 and 20. Finally, the trapezoidal rule was used to numerically integrate equation (2) over 100 points between $6.0 \times 10^{-3}$ and 5.4 meV. Figure 2 shows the experimental data[19] together with the values calculated by equations (4), (3), (2) and (1), using the potential function $E_p^{(0)}$.

The inverse procedure

The inverse problem consists of the determination of $E_p(R)$ using known viscosity data, $\eta(T)$. Therefore, one has to solve the set of four equations in the reverse sequence: (1), (2), (3) and (4). The first step provides the values of the transport cross-section, which are shown in Figure 3. This step involves equation (4), which is a linear ill-posed problem, whose solution is determined by the Tikhonov regularization method, shown in equation (5).

**Figure 3**

The result shown in Figure 3 was obtained with $\lambda = 2.5 \times 10^{-5}$ and using a matrix $K$ with dimensions of 41 (temperature) $\times$ 101 (energy). The value of $Q_0^{(2)}$ is obtained from $E_p^{(0)}$ following the direct method.

In the second part of the inverse procedure, the equations (3) and (4) are rewritten as (7), which is another linear ill-posed problem, the solution of which is provided by equation (9). Before using equation (9) to refine the potential energy function, one needs to determine the matrix $S$ from equations (10) and (12). The coupled differential equations (10) were solved using Euler’s method with initial conditions $\delta_l(R_0) = -\kappa R_0$, $S_{i_k}(R_0) = 0$ and $R_0 = 1.5$ Å. In the limit $R \to \infty$, $S_{i_k}$ is the desired sensitivity value at fixed $\kappa$, $R^*$ and $l$. Therefore, solving the coupled differential equations (9), for different values of $R^*$, $\kappa$ and $l$, we obtain the $S_{i_k}(\kappa, R^*)$ values from which, using equation (11), we calculated $S_{Q}(\kappa, R^*)$ and consequently $S$.

Now, knowing $S$, equation (9) can be used in the following manner: first, an initial guess, $E_p^{(0)}$, is given for the unknown potential, and the value of $Q_0^{(2)}$ is computed for this first potential estimation. The difference, $\Delta \ln Q^{(2)}$, is then calculated between the $\ln Q^{(2)}$ obtained from the first part and $\ln Q_0^{(2)}$. A correction to the initial potential energy function can be evaluated interactively by using equation (9). The refined potential $E_p^{(1)}$ minimizes the Tikhonov criterion function, for which the balance between the residual norm and the solution norm is given by $\lambda = 19$.

The potential curve $E_p^{(3)}$, obtained after three iterations, is shown in Figure 4 together with the reference potential $E_p$ and the initial choice $E_p^{(0)}$. The refined potential $E_p^{(3)}$ has an
average error of 2.6 % between 2.4 and 4.5 Å compared with the ab initio potential curve.\[8\] The potential depth is -11.1 K for the potential obtained in this work, while for the reference potential, the depth is -11.0 K; therefore, an error of less than 1 % is observed. The equilibrium distance is 2.96 Å for both potentials.

**Figure 4**

The viscosity coefficient was determined using refined potential $E_p^{(3)}$, this result together with experimental data are shown in Figure 2, for temperatures between 1 and 5 K. The improved potential is adequate to describe the experimental data with an average error of 1.6823 % against 12.4632 % when $E_p^{(0)}$ was used. The average error found with the $E_p^{(3)}$ potential is less than the experimental error (5 %), therefore the inverted results provided a better potential than the initial curve $E_p^{(0)}$. The potential $E_p^{(3)}$, obtained directly from the experimental data, had equivalent results when compared with the ab initio potential presented in reference,\[8\] in which the average error is 1.1173 %. Both the refined potential $E_p^{(3)}$ and the ab initio potential $E_p$[8] are in agreement with the experimental value, with errors less than the experimental errors. Therefore, both potential curves, $E_p^{(3)}$ and $E_p$, are equally suitable to describe the viscosity coefficient between 1 and 5 K.

## 4 Conclusions

The long range potential function for helium was determined in the present work from viscosity coefficient data at temperatures below 5 K. To the best of our knowledge, this approach has never been reported. In this case, quantum assumptions and the Bose-Einstein statistic are required to connect viscosity coefficient with interatomic potential. This relationship is nonlinear, and a common method to solve this inverse problem cannot be employed. To circumvent this difficulty, the sensitivity matrix was used to linearize this problem. The initial problem was rewritten as a linear Fredholm integral equation of the first order, whose solution is given by the Tikhonov method. The success of the proposed method depends on finding a cross-section sensitivity matrix by a consistent and robust procedure.

In a previous work,\[5\] a differential equation for the functional derivative of the quantum phase shift with respect to the potential energy was established and coupled to Calogero’s equation. In the present work, this previous result was used to establish the cross-section sensitivity matrix within exact quantum theory, for the first time.
Finally, the long range potential curve was obtained from experimental data and compared with recent \textit{ab initio} potentials\cite{8} showing an excellent agreement. The average difference between both is less than 2.6 \% between 3 and 4 Å, with an even smaller difference in the potential depth, -11.1 K against -11.0 K. The potential depth is important result, which shows that there is excellent agreement with a bound state prediction of the $^4\text{He}$ dimer\cite{7}. The refined potential describes the viscosity coefficient with an average error of 1.6823 \% that is less than the experimental error (5 \%), a result similar to that found for the \textit{ab initio} potential (1.1173 \%).

The present algorithm is general and can be used to determine the potential energy function whenever \textit{ab initio} calculations cannot be used. The method could be applied without difficulty to an inverted second virial coefficient or other transport properties at low temperatures when quantum assumptions are needed.

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\section*{References}

\begin{enumerate}
\item H. E. Cox, F. W. Crawford, E. B. Smith and A. R. Tindell, \textit{Mol. Phys.}, 1980, \textbf{40}, 705-712.
\item N. H. T. Lemes, R. C. O. Sebastião and J. P. Braga, \textit{Inverse Probl. Sci. Eng.}, 2006, \textbf{14}, 581-587.
\item T. Ho and H. Rabitz, \textit{J. Chem. Phys.}, 1989, \textbf{90}, 1519-1525.
\item N. H. T. Lemes, E. Borges, R. V. Souza and J. P. Braga, \textit{Int. J. Quantum Chem.}, 2008, \textbf{108}, 2623-2627.
\item N. H. T. Lemes, J. P. Braga, M. O. Alves and É. D’M. Costa, \textit{J. Mol. Model}, 2014, \textbf{20}, 2317.
\item W. Cencek, M. Przybytek, J. Komasa, J. B. Mehl, B. Jeziorski, K. Szalewicz, \textit{J. Chem. Phys.}, 2012, \textbf{136}, 224303.
\item É. D’M. Costa, N. H. T. Lemes, M. O. Alves, R. C. O. Sebastião and J. P. Braga, \textit{J. Braz. Chem. Soc.}, 2013, \textbf{24}, 363-368.
\item A. J. C. Varandas, \textit{J. Phys. Chem. A}, 2010, \textbf{114}, 8505-8516.
\end{enumerate}
[9] M. Przybytek, W. Cencek, J. Komasa, G. Lach, B. Jeziorski, and K. Szalewicz, *Phys. Rev. Lett.*, 2010, **104**, 183003. Erratum, *Phys. Rev. Lett.*, 2012, **108**, 129902.

[10] G. C. Maitland, *Intermolecular forces: their origin and determination*, Oxford University Press, London, 1981.

[11] S. U. Kim and C. W. Monroe, *J. Comput. Phys.*, 2014, **273**, 358-373.

[12] K. Pachucki and J. Komasa, *J. Chem. Phys.*, 2006, **124**, 064308.

[13] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases: An Account of the Kinetic Theory of Viscosity, Thermal Conduction and Diffusion in Gases*, Cambridge University Press, Cambridge, 1953.

[14] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1964.

[15] V. D. Viterbo, N. H. T. Lemes and J. P. Braga, *Rev. Bras. Ensino Fis.*, 2014, **36**, 1310.

[16] J. P. Braga, and J. N. Murrell, *Mol. Phys.*, 1984, **53**, 295-299.

[17] E. W. Becker, R. Misenta and F. Schmeissner, *Z. Phys.*, 1954, **137**, 126-136.

[18] E. Bich, R. H. and E. Vogel, *Mol. Phys.*, 2007, **105**, 3035-3049.

[19] P. J. Nacher, *J. Chem. Phys.*, 1994, **101**, 6367-6368.

[20] M. Keil and L. J. Danielson, *Can. J. Phys.*, 1988, **66**, 159-163.
Figures

Figure 1: Level curves: (a) for the normalized cross-section sensitivity matrix and (b) for the normalized viscosity sensitivity matrix.
Figure 2: Viscosity coefficients of $^4$He: (squares) the experimental data from Becker et al.,[17] (asterisks) the calculated data from Cencek et al.,[6] (solid curve) the data generated with equation (15), (dashed curve) the data calculated with $E_p^{(0)}$ and (dotted curve) the data calculated with $E_p^{(3)}$. 
Figure 3: Inverted cross section.

Figure 4: Interatomic potentials: (solid curve) the reference potential energy function, (dashed curve) the initial guess and (dotted curve) from this work.