A TEMPERATURE DEPENDENT MORSE-LIKE POTENTIAL FOR AN INEXPENSIVE YET ACCURATE PREDICTION OF THERMAL EXPANSION IN SOLIDS

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Abstract: Energy potential functions are developed within a (semi-)empirical framework, with the main purpose of simplifying the complexity of quantum mechanics based computation, such as *ab initio* calculations. These functions return a value of energy based on the displacement of particles in space.

Keywords: Temperature-Dependent Morse Potential; Thermal Expansion Coefficients; Matrix Elements; Hypervirial Theorem; Second Quantisation.

Some potentials such as the Morse potential[1,2] and embedded-atom method (EAM)[3] were developed and proposed to describe the potential energy function between atoms in molecules and crystals, and in particular in metals. The Morse potential,

$$\Phi(r) = D_e\left[e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}\right],$$

is a three-parameter empirical potential that attempts to include the description of the phenomenon of the dissociation beyond a certain energy value D_e and the asymmetry of the interaction. Despite their orthogonality, the Morse wave functions do not form a non-complete set of functions, due to the fact that the number of wave functions (and energy levels) is finite; as said, beyond a certain energy level, the dissociation of the system occurs and the states are no longer bonded. However, this potential acquired a historical importance, since it represents the first case of analytical solution of the time-independent Schrödinger equation with a finite number of eigenstates. They have been successfully applied in a number of cases to estimate properties of metals at room temperature in many articles.[4] In particular, anharmonic interatomic potentials including Morse potential parameters have been intensively studied since the late 1950s.[2,4,5] They are used for the calculation and analysis of the thermodynamic parameters, especially, the anharmonic effects contained in XAFS (X-ray Absorption Fine Structure),[5] which influence on the physical information taken from these spectra. The anharmonicity is also included in refined calculations of vibrational (IR and Raman) and vibronically resolved electronic spectra. Nonetheless, these types of calculations are so expensive and time-consuming from a computational point of view to be inapplicable to middle-large size molecular systems.

Concerning the description and prediction of thermal and mechanical behaviour of solids, some difficulties arise when temperature condition deviates from room temperature. It is well-known that temperature causes the phenomenon of thermal expansion, which is a temperature-dependent behaviour derived by the anharmonicity of the interatomic potential. In other words, if we assume that interactions between particle of a crystal are described by the harmonic potential deriving from the classical Hooke law,

$$\Phi(r) = \tfrac{1}{2}k(r-r_e)^2,$$

the thermal expansion of the solid could not be described, since $\langle r \rangle = r_e$, being the potential even. Moreover, other material characteristics of solids, such as elastic constant and heat capacity, also vary with temperature due to the nature of anharmonic vibrations. Furthermore, molecular or atomic

bonding strengths are presented after taking the differentiation of the potential function. Bonding strengths are the key factors of the mechanical properties of bulk materials.

This study is focused on two main aspects. Firstly, some fundamental developments related with the evaluation of matrix elements between Morse wave functions are presented. Since the analytical expressions are derived, this approach is fast to evaluate and does not require great computational efforts. Furthermore, thanks to these formulae, we were able to show some key aspect of the behaviour of systems when populate their zeroth vibrational level. Numerical example are shown and discussed. In the second part of this work, an application of the previous theoretical development is shown. This consists of a simple atomic-level model for the estimation of temperature-dependent thermal expansion coefficients of bulk metals. The latter is applied to a series of metals. This model provides an efficient and rapid way for evaluating material characteristics once the parameters of the Morse potential function and temperature are known. A temperature-dependent modified Morse potential is finally developed and validated.

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ВЛИЯНИЕ ЩЕЛОЧНОЗЕМЕЛЬНЫХ МЕТАЛЛОВ НА ТЕПЛОЁМКОСТЬ И ИЗМЕНЕНИЕ ТЕРМОДИНАМИЧЕСКИХ ФУНКЦИЯ СПЛАВА АК1М2 НА ОСНОВЕ ОСОБОЧИСТОГО АЛЮМИНИЯ

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Аннотация: известно, что особочистий алюминий с минимальным содержанием примесей широко используется в электронной технике для изготовления токопроводящих дорожек интегральных микросхем. Отсюда разработка новых составов сплавов на основе такого металла является весьма актуальной задачей. Одним из перспективных сплавов на основе такого металла является сплав АК1М2 (Al+1%Si+2%Cu). Данный сплав был принять нами в качестве модельного сплава и подвергался модифицированию щелочноземельными металлами.

Теплоёмкость является важнейшей характеристикой веществ и по её изменению от температуры можно определить тип фазового превращения, температуру Дебая, энергию образования вакансий, коэффициент электронной теплоёмкости и др. свойства. В настоящей работе теплоёмкость сплава АК1М2 с щелочноземельными металлами определялось в режиме «охлаждения» по известной теплоёмкости эталонного образца из меди. Для чего обработкой кривых скорости охлаждения образцов из сплава АК1М2 с щелочноземельными металлами и эталона получены полиномы описывающие их скорости охлаждения. Далее, по экспериментально найденным величинам скоростей охлаждения эталона и образцов из сплавов, зная их массы, были установлены полиномы температурной зависимости теплоемкости сплавов и эталона, которые описываются четырёхчленным уравнением. Используя, интегралы от удельной теплоемкости были установлены модели температурной зависимости изменение энтальпии, энтропии и энергии Гиббса.