JOURNAL OF COMPUTATIONAL PHYSICS 12, 308–314 (1973)

A Numerical Method for Calculating the Spatial Distribution Function of Quantum Statistical Thermodynamics*

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Received July 28, 1972

The Schrödinger equation is used to derive a linear partial differential equation which forms the basis of a numerical method for computing the temperature—dependent spatial distribution function of quantum statistical thermodynamics. The numerical method is used to calculate the spatial distribution function including quantum effects over a wide range of temperatures. The advantages of employing this numerical method are discussed.

INTRODUCTION

The calculation of the spatial distribution function for a wide range of temperatures is one of the more difficult problems in the field of quantum statistical thermodynamics. The direct method of obtaining the spatial distribution function at a given temperature consists of solving the Schrödinger equation

$$-(\hbar^2/2m)\,\psi_n'' + V(x)\,\psi_n(x) = E_n\psi_n(x), \tag{1}$$

for the wave functions $\psi_n(x)$ for all the quantum states and then evaluating the sum [1]

$$S(x, \beta) = \sum_n |\,\psi_n(x)|^2 \exp(-\beta E_n), \tag{2}$$

where $\beta = 1/kT$ is the reciprocal temperature, and $\sum_n$ denotes a complete summation over all states including an integration over the continuous part of the spectrum. Expression (2), which is frequently referred to as the Slater sum, has been the subject of important investigations [2–4]. In several cases, the series (2) has been summed to give an analytic expression for $S(x, \beta)$. One such case occurs

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* Research supported in part by a grant from the National Science Foundation.

for the harmonic oscillator potential $V(x) = m\omega^2 x^2/2$, for which the wave functions are related to Hermite polynomials. Using a theorem on the sum of products of Hermite polynomials, Uhlenbeck, Ornstein, and Gropper [5, 6] obtained

$$S(x, \beta) = \left[\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)}\right]^{1/2} \exp[-(m\omega x^2/\hbar) \tanh(\beta\hbar\omega/2)]. \tag{3}$$

This expression for the Slater sum is valid for all temperatures. Unfortunately, only a few such results have been obtained to date.

It is the purpose of this paper to use the Schrödinger equation to derive directly a partial differential equation for the spatial distribution function $S(x, \beta)$, and then to employ this result to obtain a method for calculating numerical solutions for $S(x, \beta)$.

PARTIAL DIFFERENTIAL EQUATION

The probability density of quantum mechanics is given by the relation

$$P(x) = \phi(x)\,\psi(x), \tag{4}$$

where $\phi(x)$ is the complex conjugate of the wave function $\psi(x)$. The first and second derivatives of the probability density are

$$P' = \phi'\psi + \phi\psi', \tag{5}$$

$$P'' = 2\alpha P + 2\phi'\psi'. \tag{6}$$

To derive (6) we have used the Schrödinger equation

$$\psi'' = \alpha\psi, \tag{7}$$

where

$$\alpha(x) = (2m/\hbar^2)[V(x) - E]. \tag{8}$$

Differentiating (6), we obtain

$$P''' = 2\alpha P' + 2\alpha' P + 2\alpha[\phi'\psi + \phi\psi']. \tag{9}$$

Combining (5) and (9) yields a linear differential equation for the probability density

$$P''' = 4\alpha P' + 2\alpha' P. \tag{10}$$

Equation (10) can be written in the form

$$\frac{\hbar^2}{8m} P''' + [E - V(x)]\,P' - (1/2)\,V'P(x) = 0. \tag{11}$$

Multiplying (11) by $\exp(-\beta E_n)$, summing over all states, using (2) and noting that

$$\frac{\partial S}{\partial \beta} = -\sum_n E_n P_n(x) \exp(-\beta E_n), \tag{12}$$

we obtain a linear partial differential equation for $S(x, \beta)$:

$$\frac{\hbar^2}{8m}\frac{\partial^3 S}{\partial x^3} - \frac{\partial^2 S}{\partial x\, \partial \beta} - V(x)\frac{\partial S}{\partial x} - (1/2)\, V' S(x, \beta) = 0. \tag{13}$$

If $V(x)$ is the harmonic oscillator potential, it is readily confirmed that (3) satisfies (13). The partial differential equation (13) was derived previously [7] by linearizing Bohm's nonlinear equation for the probability density [8].

INTEGRAL EQUATION AND NUMERICAL SOLUTIONS

A convenient form of (13) is obtained by integrating (13) from a boundary point x_0 to an interior point x:

$$\begin{aligned}(\hbar^2/8m)\, \partial^2 S/\partial x^2 - \partial S/\partial \beta &= V(x)\, S(x, \beta) - (1/2) \int_{x_0}^{x} V'(y)\, S(y, \beta)\, dy \\ &+ (\hbar^2/8m)[\partial^2 S(x_0, \beta)/\partial x^2] - \partial S(x_0, \beta)/\partial \beta + V(x_0)\, S(x_0, \beta). \end{aligned}\tag{14}$$

The values of the three inhomogeneous terms on the right hand side of (14) are determined by the boundary condition at x_0. For example, if x_0 is the position of an atom of mass m far from an adsorbing surface, the Slater sum has the form

$$S(x_0, \beta) = (m/2\pi\hbar^2\beta)^{1/2}, \tag{15}$$

and (14) becomes

$$\begin{aligned}&(\hbar^2/8m)\, \partial^2 S/\partial x^2 - \partial S/\partial \beta \\ &\quad = V(x)\, S(x, \beta) - (1/2) \int_{x_0}^{x} V'(y)\, S(y, \beta)\, dy - (m/8\pi\hbar^2\beta^3)^{1/2}\end{aligned} \tag{16}$$

Another convenient equation for calculating the spatial distribution function can be derived by considering $S(x, \beta)$ to be equal to the sum of the classical spatial distribution function $S_c(x, \beta)$ plus a quantum correction term $R(x, \beta)$,

$$S(x, \beta) = S_c(x, \beta) + R(x, \beta), \tag{17}$$

where

$$S_c(x, \beta) = (m/2\pi\hbar^2\beta)^{1/2} \exp[-\beta V(x)]. \tag{18}$$

Substituting (17) into (16) yields

$$\begin{aligned}(\hbar^2/8m)\,\partial^2 R/\partial x^2 - \partial R/\partial\beta \\ = V(x)\,R(x,\beta) - (1/2)\int_{x_0}^{x} V'(y)\,R(y,\beta)\,dy - (\hbar^2/8m)\,\partial^2 S_c/\partial x^2,\end{aligned} \tag{19}$$

where

$$\partial^2 S_c/\partial x^2 = (m/2\pi\hbar^2\beta)^{1/2}\,[\beta^2(V')^2 - \beta V''(x)]\exp[-\beta V(x)]. \tag{20}$$

The two terms on the left hand side of (16) or (19) have the form of the diffusion equation with x and β as the independent variables. In solving (16) or (19) numerically, this fact led us to use a Crank–Nicholson operator [9] for the left hand side of (16) or (19). A modified Picard iteration method [10] was employed to treat the integral on the right hand side numerically. The numerical procedure consisted of starting the computer program in the high temperature region at β_0 with the

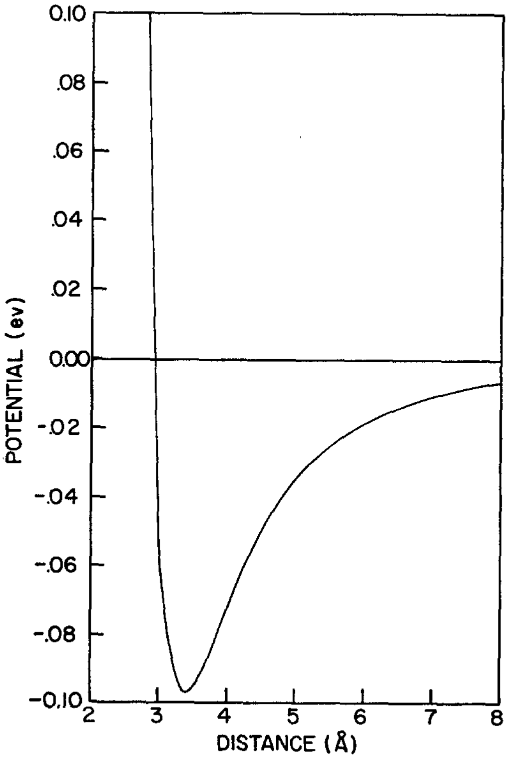

Fig. 1. Potential energy between an argon atom and a graphite surface.

classical distribution function given by (18) and using the Crank–Nicholson operator and the modified Picard iteration method to compute the spatial distribution function at $\beta_0 + \Delta\beta$. From the value of the spatial distribution function at $\beta_0 + \Delta\beta$, the value of the spatial distribution function at $\beta_0 + 2\Delta\beta$ was then similarly computed. The numerical procedure was continued until the spatial distribution function was calculated at the desired value of β. In addition, to check the accuracy of the results, the calculations were repeated with smaller $\Delta\beta$ steps and smaller Δx steps. The proper operation of the computer program was confirmed by calculating the spatial distribution function $S(x, \beta)$ for a harmonic oscillator potential and establishing that the numerical results agreed with the exact analytical expression (3).

Next we considered the problem of calculating the spatial distribution function of an argon atom interacting with a graphite surface. The potential energy between the argon atom and the carbon atoms of the graphite lattice was calculated by the

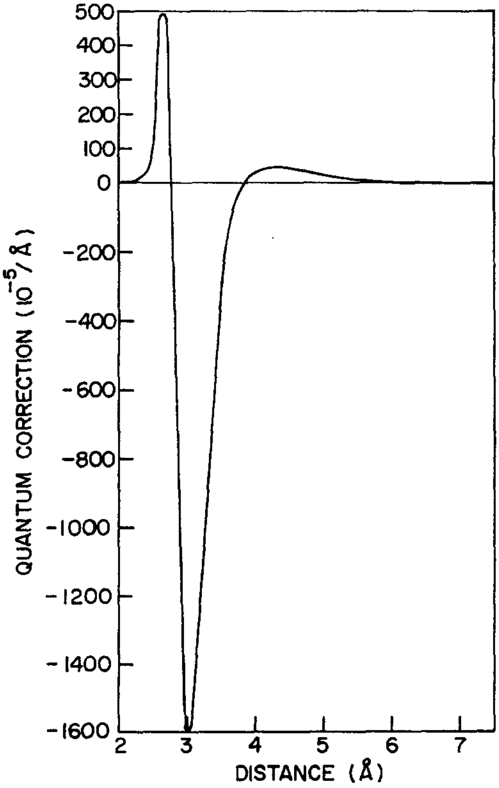

FIG. 2. Quantum correction $R(x,\beta)$ to the classical spatial distribution function at $\beta = 8.0\ \text{ev}^{-1}$.

method of Crowell [11] and the results are shown in Fig. 1. The quantum correction $R(x, \beta)$ as a function of distance at reciprocal temperatures $\beta = 8.0\ \mathrm{ev}^{-1}$ and $\beta = 31.0\ \mathrm{ev}^{-1}$ as obtained from the computer program for (19) are shown in Figs. 2 and 3, respectively.

The advantages of using (16) or (19) to calculate $S(x, \beta)$ rather than (2) become obvious when one considers what is involved in evaluating (2). First, we would have to solve the Schrödinger equation (1) numerically for all the eigenfunctions. This is especially difficult for the higher eigenfunctions, which have many oscillations. Assuming that this could be done, we would still have the problem of evaluating the infinite sum (2).

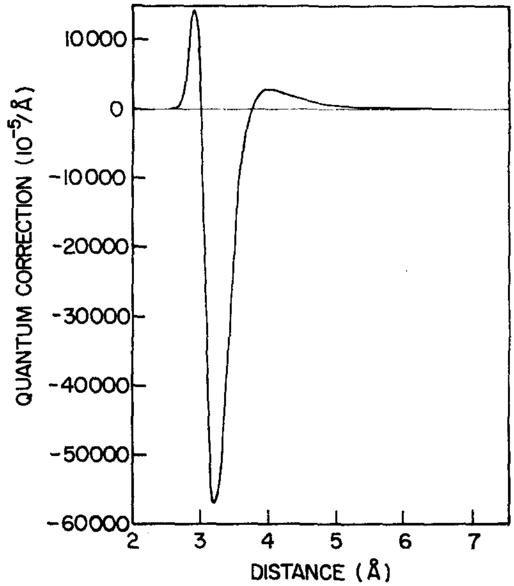

Fig. 3. Quantum correction $R(x, \beta)$ to the classical spatial distribution function at $\beta = 31.0\ \mathrm{ev}^{-1}$.

Acknowledgments

The support of this research by the National Science Foundation is acknowledged. In addition, this work made use of computer facilities supported in part by National Science Foundation Grants NSF-GJ-34 and NSF-GU-3157.

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