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Application of the virial theorem for improving eigenvalue calculations of multiparticle systems

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ABSTRACT

The virial theorem is a fundamental property for multiparticle systems in quantum mechanics, and offers an elegant relationship between kinetic and potential energies of quantum states. In this paper, we study applications of the virial theorem for improving eigenvalue calculations of multiparticle systems. We propose the *virial steepest descent scheme* and the *two-point linear extrapolation*, to improve the accuracy of such eigenvalue calculations through post-processing eigenvalue data obtained from standard methods. Mathematical analysis of both methods is presented. Examples are included to illustrate the efficiency of both methods.

1. Introduction

The virial theorem is a fundamental property in mechanics, stating that the time average of the kinetic energy of a system of particles equals to the "virial" of the external forces and the forces between particles. The word "virial" is derived from *vis*, the Latin word for "force" or "energy", introduced first by Clausius [1] in 1870. When the forces are derivable from a potential, which is homogeneous of degree n, the "virial" is simply the time average of the potential multiplied by a factor $n/2$, and the virial theorem takes a particularly simple form. The direct analogy of the virial theorem in quantum mechanics was studied by Born, Heisenberg and Jordan [2] in 1926, Finkelstein [3] in 1928, Hylleraas [4] in 1929 and Fock [5] in 1930. Variants of the virial theorem are also known, such as a variational form by Ledoux [6], a tensor form by Parker [7], and a sharp form by Pollard [8]. Applications of the virial theorem are rather notable in chemical physics [9,10] and astrophysics, e.g., as a tool for estimating the mass of a galaxy [11].

The calculation of eigenvalues of elliptic partial differential operators on $\mathbb{R}^N$ is ubiquitous in many applications of quantum mechanics. For example, the Schrödinger equation with a *Coulomb potential* is used to model atomic or molecular systems. The total energy E includes *kinetic energy* K and *potential energy* P, $E = K + P$. The determination of *energy levels* of *ground state* and *excited states* is crucial in quantum chemistry. Such levels correspond exactly to the eigenvalues of the

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Schrödinger operator. The virial theorem gives an elegant relation between kinetic and potential energies: $2K + P = 0$ or $P/K = -2$. In order to compute the energy levels of a multiparticle system by methods such as finite element methods, the unbounded domain needs to be truncated inevitably down to a bounded domain. Assume that E_h, K_h and P_h are the corresponding numerical values, where h denotes the discretization parameter. Then $E_h = K_h + P_h$. If the ratio P_h/K_h deviates very much from -2, then we know *a priori* in general that numerical eigenvalue E_h cannot be very accurate. In this sense, the virial theorem provides a useful means for assessing the quality of numerical results or even numerical methods.

A natural question is: can the virial theorem be utilized in an even more constructive way to improve the accuracy of numerical eigenvalue calculations? In 1959, Löwdin [12] addressed this problem by using a scaling transformation. He showed that one can find a suitable scale factor η such that $\phi_\eta(\boldsymbol{r}) = \phi(\eta\boldsymbol{r})$ fulfills the virial theorem for a given numerical solution $\phi(\boldsymbol{r})$ of the Schrödinger equation. Löwdin found that *the satisfaction of the virial theorem is a necessary but not sufficient criterion that a wave function is an accurate solution of the Schrödinger equation*, but may *render a certain improvement in the energy*. Nevertheless, Löwdin's paper did not seem to have drawn much attention from the quantum mechanics and mathematical physics communities. Except a paper [13] by Magnoli and Murdoch, little work has been done along this direction in the existing literature. Moreover, even though the virial theorem is somewhat or reasonably familiar to researchers in the quantum mechanics and mathematical physics communities, it is obviously not so to those doing scientific computation and other branches of applied mathematics. The objective of this paper is to present a new numerical scheme based on the virial theorem to improve the accuracy of numerical eigenvalues.

The organization of the paper is as follows. In Section 2, we give a brief introduction of some basic properties of the Schrödinger operator and the virial theorem in order to make the paper sufficiently self-contained. In Section 3, we introduce first Löwdin's idea of scaling for utilizing the virial theorem in eigenvalue computation. Then we propose a new scheme, called *virial steepest descent*, to improve the accuracy of numerical eigenvalues. In Section 4, we present another idea, *two-point linear extrapolation*, to improve the accuracy of numerical eigenvalues. Numerical examples are given in Section 5 to illustrate the effectiveness of both schemes.

2. The virial theorem in quantum mechanics

Consider the Schrödinger equation in non-relativistic quantum mechanics:

$$i\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{r},t) = \mathcal{H}\psi(\boldsymbol{r},t), \quad t > 0, \tag{2.1}$$

where $\hbar > 0$ is the Planck constant, $\boldsymbol{r} = (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \in \mathbb{R}^{3N}$ is the collective position vector of N particles, with $\boldsymbol{r}_j$ denoting the position of the jth particle in $\mathbb{R}^3$. The Schrödinger operator $\mathcal{H}$ in (2.1) is given by

$$\mathcal{H} = \sum_{j=1}^{N}\frac{p_j^2}{2m_j} + V(\boldsymbol{r}), \tag{2.2}$$

where $p_j = -i\hbar\nabla_j$, and m_j is the mass of the jth particle. Potential $V(\boldsymbol{r})$ is a real-valued function defined on $\mathbb{R}^{3N}$. A typical example of $V(\boldsymbol{r})$ is the *Coulomb potential* for an atom with N electrons,

$$V(\boldsymbol{r}) = \sum_{1\le k<\ell\le N}\frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}_\ell|} - \sum_{k=1}^{N}\frac{Z}{|\boldsymbol{r}_k|}, \tag{2.3}$$

where Z denotes the nuclear charge. The electronic wave function $\psi(\boldsymbol{r},t)$ in (2.1) satisfies the normalization condition

$$\int_{\mathbb{R}^{3N}} |\psi(\boldsymbol{r},t)|^2 d\boldsymbol{r} = 1,$$

signifying that $|\psi(\boldsymbol{r},t)|^2$ is the probability density for finding the particle at $(\boldsymbol{r},t)$. Through this paper, the spin variables and the Pauli exclusion principle are ignored. There is no additional constraint of antisymmetry on wave function $\psi(\boldsymbol{r},t)$. Let

$$\psi(\boldsymbol{r},t) = e^{-iEt/\hbar}\psi(\boldsymbol{r}), \quad t > 0.$$

Then (2.1) becomes

$$\mathcal{H}\psi(\boldsymbol{r}) = \left(-\frac{1}{2}\sum_{j=1}^{N}\frac{\hbar^2}{m_j}\nabla_j^2 + V\right)\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}). \tag{2.4}$$

The Schrödinger equation (2.4) constitutes a second order linear elliptic eigenvalue problem on the whole space $\mathbb{R}^{3N}$. Since $\mathcal{H}$ is a Hermitian operator, all eigenvalues and eigenstates of $\mathcal{H}$ are real. Introduce the following bilinear form

$$\begin{aligned} a(u,v) &\equiv \sum_{j=1}^{N}\frac{\hbar^2}{2m_j}\int_{\mathbb{R}^{3N}}\nabla_j u\cdot\nabla_j v\,d\boldsymbol{r} + \int_{\mathbb{R}^{3N}} Vuv\,d\boldsymbol{r}, \\ &\equiv a_K(u,v) + a_P(u,v), \quad u,v\in H^1(\mathbb{R}^{3N}). \end{aligned} \tag{2.5}$$