Comment on: "Split kinetic energy method for quantum systems with competing potentials", Ann. Phys. 327 (2012) 2061

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ABSTRACT

We show that the kinetic-energy partition method (KEP) is a particular example of the well known Rayleigh–Ritz variational method. We discuss some of the KEP results and compare them with those coming from other approaches.

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1. Introduction

Mineo and Chao [1] proposed an approach for solving the time-independent Schrödinger equation for systems with competing potentials which means that the Schrödinger equation for each of the potentials is exactly solvable. The method consists in writing the solution to the Schrödinger equation as a linear combination of two basis sets, one for each potential. To this end, the authors split the kinetic energy into two parts so that the whole Hamiltonian operator is a sum of two operators that depend on the same momentum and coordinate.

They applied the above-mentioned kinetic energy partition (KEP) strategy to three quantum-mechanical models: a sort of one-dimensional delta-potential molecule, a charged harmonic oscillator in a strong magnetic field and the hydrogen-molecule ion under the Born–Oppenheimer approximation. The first two models are exactly solvable.

The purpose of this comment is to analyze both the method as well as its applications to these illustrative quantum-mechanical models. In Section 2 we outline KEP, in Section 3 we discuss its application to three illustrative examples and compare it with other approaches and in Section 4 we summarize the main results and draw conclusions.

2. Outline of KEP

As sketched in the introduction KEP applies to a Hamiltonian of the form

$$H = T + V_1 + V_2. \tag{1}$$

It consists in splitting the kinetic energy as $T = T_1 + T_2$ and solving the Schrödinger equations for the Hamiltonians $H_i = T_i + V_i$. The approximate solution for H is then written as a linear combination of the eigenfunctions of these two operators.

$$\psi = \sum_n C_{1n}\psi_{1n} + \sum_k C_{2k}\psi_{2k},$$

$$H_i\psi_{ij} = E_{ij}\psi_{ij}, \ i = 1, 2. \tag{2}$$

The coefficients C_{ij} and the approximate eigenvalues of H are then obtained from the conditions

$$\langle\psi_{1i}| H - E |\Psi\rangle = 0,$$

$$\langle\psi_{2j}| H - E |\Psi\rangle = 0, \tag{3}$$

that lead to the secular equations which one would obtain by means of the well known Rayleigh–Ritz variational method with the basis set $\{\psi_{1i}, \psi_{2j}, i, j = 1, 2, \ldots\}$. In other words, KEP is a Rayleigh–Ritz variational approach with an overcomplete basis set (see [2] for details on the problems of such basis sets). According to the authors this is "a general solution scheme" but the obvious fact is that it is restricted to problems where one can solve the Schrödinger equation for each H_i exactly. It is clear that this approach cannot be applied to most problems of physical interest (as we can certainly do with the more general Rayleigh–Ritz method). The authors applied KEP to three examples that we analyze in the following section.

3. Illustrative examples

The Schrödinger equation for the one-dimensional delta-potential molecule is

$$-\frac{\hbar^2}{2m}\psi''(x) - \lambda\left[\delta(x+a) + \delta(x-a)\right]\psi(x) = E\psi(x), \tag{4}$$

where $\delta(x)$ is the well known Dirac delta function. If we define

$$q = \frac{x}{a}, \ \epsilon = \frac{ma^2}{\hbar^2}E, \ Z = \frac{ma\lambda}{\hbar^2}, \tag{5}$$

we obtain the much more convenient dimensionless equation

$$-\frac{1}{2}\varphi''(q) - Z\left[\delta(q+1) + \delta(q-1)\right]\varphi(q) = \epsilon\varphi(q). \tag{6}$$

After solving this equation in the usual way we obtain the following two solutions

$$Z = \frac{ke^{2k}}{e^{2k}+1}, \ Z = \frac{ke^{2k}}{e^{2k}-1}, \ k = \sqrt{-2\epsilon}. \tag{7}$$

The first solution is the ground state that is bound for all values of $Z > 0$ and the second one is the excited state bound only for $Z > \frac{1}{2}$. These analytic parametric solutions are quite practical for many purposes.

In what follows we compare the KEP solution with the textbook approach known as molecular orbital as linear combination of atomic orbitals (MOLCAO). To this end we define the dimensionless kinetic and potential-energy operators

$$T = -\frac{1}{2}\frac{d^2}{dq^2}, \ V_1(q) = -Z\delta(q+1), \ V_2(q) = -Z\delta(q-1), \tag{8}$$

and

$$U_1(q) = k\delta(q+1), \ U_2(q) = k\delta(q-1), \tag{9}$$

where k is an adjustable parameter.

Note that

$$f_1(q) = \sqrt{k}e^{-k|q+1|}, \ f_2(q) = \sqrt{k}e^{-k|q-1|}, \tag{10}$$

are eigenfunctions of $T + U_1$ and $T + U_2$, respectively. The MOLCAO consists of using the variational ansatz $\varphi(q) = c_1 f_1(q) + c_2 f_2(q)$. Because of symmetry we know that $c_1 = \pm c_2$ and the two approximate (unnormalized) Rayleigh–Ritz solutions are given by

$$\varphi_\pm = f_1 \pm f_2, \tag{11}$$

with which we obtain the approximate energies

$$\epsilon_\pm = \frac{\langle\varphi_\pm| H |\varphi_\pm\rangle}{\langle\varphi_\pm| \varphi_\pm\rangle} = \frac{H_{11} \pm H_{12}}{1 \pm S_{12}}, \tag{12}$$

where

$$H_{11} = -\frac{k^2}{2} + (k-Z)k - Zke^{-4k},$$

$$H_{12} = -\frac{k^2}{2}S_{12} + (k-Z)ke^{-2k} - Zke^{-2k},$$

$$S_{12} = \langle f_1| f_2\rangle = (2k+1)\,e^{-2k}. \tag{13}$$

The optimal parameter k for each of the states can be obtained as a root of the variational condition $\partial\epsilon_\pm/\partial k = 0$. Here we solve each variational condition for $Z(k)$ that we then substitute into the corresponding $\epsilon_\pm$ in order to obtain $\epsilon_\pm(k)$. The result is

$$Z = \frac{ke^{2k}}{e^{2k}+1}, \ \epsilon_+ = -\frac{k^2}{2}, \tag{14}$$

for the ground state and

$$Z = \frac{ke^{2k}}{e^{2k}-1}, \ \epsilon_- = -\frac{k^2}{2}, \tag{15}$$

for the excited one. Note that the well known MOLCAO yields the exact energies of the delta-potential molecule (7). The parameter k plays the role of an effective nuclear charge that depends on $Z(m, a, \lambda)$. On the other hand KEP only provides an approximate result for the ground state and, according to the authors, does not give the excited state at all: "Here the minus sign is excluded because it yields an unbound state"[1].

The second example is trivial and we just outline it for completeness. In the case of a charged harmonic oscillator in a strong magnetic field the resulting potentials $V_1(\rho)$ and $V_2(\rho)$, $\rho^2 = x^2 + y^2$, are harmonic. Therefore, $V(\rho) = V_1(\rho) + V_2(\rho)$ is harmonic and the Schrödinger equation exactly solvable. Clearly, in this case there is no need of an approximate method and solving the Schrödinger equation for $T + V$ is as simple as solving the one for each $T_i + V_i$.

The third example, the hydrogen-molecule ion, is by far more interesting. In principle, we can view (4) as a sort of oversimplified one-dimensional version. Apparently, the authors write the Hamiltonian
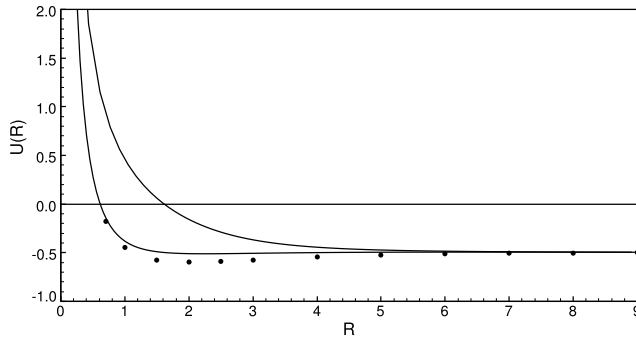
Fig. 1. Ground state ($\sigma_g 1s$) and first-excited state ($\sigma_u 1s$) of the H_2^+ molecule. Continuous lines and filled circles indicate MOLCAO and Gaussian [3] results.

in the Born–Oppenheimer approximation and atomic units as

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r_1} - \frac{1}{r_2}, \tag{16}$$

and split the energy as

$$T = T_1 + T_2, \ T_1 = -\frac{1}{2\alpha}\nabla^2, \ T_2 = -\frac{1}{2}\left(1 - \frac{1}{\alpha}\right)\nabla^2, \tag{17}$$

where α is a function of the internuclear distance $R = \left|\vec{r}_1 - \vec{r}_2\right|$. Here the notation becomes confusing because the authors also write $r_i = \left|\vec{r} - \vec{r}_i\right|$ and $\vec{r}_1 + \vec{r}_2 = 0$. Note that these vector expressions are inconsistent.

The authors claimed that they applied KEP with a linear combination of $1s$ and $2s$ solutions to the equations $H_i\psi_{in} = E_{in}\psi_{in}$, $i = 1, 2$, and obtained reasonably accurate results. Unfortunately, they forgot to say how they determined the dependence of α on R. If they resorted to the variational principle, then the resulting approach is a variant of MOLCAO with four atomic orbitals and an effective nuclear charge related to α. In other words, it would be a Rayleigh–Ritz method with a nonlinear variational parameter. If, on the other hand, they just set α in order to fit the Gaussian results [3] then such an application of KEP is of no practical utility.

According to the authors, the simplest MOLCAO discussed by Levine [4] yields poor results. It is not clear to us how they carried out such calculation. The fact is that if one takes into account the variational effective nuclear charge proposed in that book the results are considerably more accurate (see the pedagogical article by Castro et al. [5] for more details). Fig. 1 shows the ground-state and first-excited-state energies as functions of R, together with the more accurate results reported by Bowen and Linnett [3]. It is clear that although MOLCAO is not extremely accurate it is in fact much more accurate than Mineo and Chao suggested. Besides, it should be taken into consideration that the simplest MOLCAO is based on a minimal basis set of two $1s$ orbitals, one on each nucleus, while the approach suggested by Mineo and Chao uses two atomic orbitals on each nucleus. In addition to it, the MOLCAO is completely self consistent because the effective nuclear charge is determined by the variational method [4,5], whereas there is no indication whatsoever about how the adjustable KEP parameter $\alpha(R)$ was set. It is also worth noting that the simplest MOLCAO yields also the first excited state, whereas Mineo and Chao only obtained the ground state by means of KEP. A straightforward MOLCAO with two $1s$ and two $2s$ atomic orbitals with suitable effective nuclear charges is expected to yield considerably more accurate results.

4. Conclusions

In this comment we have shown that KEP is the well known Rayleigh–Ritz variational method with an overcomplete basis set. Our results indicate that MOLCAO with an effective variational nuclear

charge gives the two energy eigenvalues of the delta-potential version of the H_2^+ molecule. On the other hand, KEP only provides an approximation to the ground state that deteriorates as λ increases. It is curious that in this case the authors did not try a splitting strategy similar to the one employed in the case of the actual H_2^+ molecule. The second application of KEP is quite unnecessary because the straightforward exact solution of the Schrödinger equation is considerably simpler. The H_2^+ molecule in the Born–Oppenheimer approximation, although the simplest nonrelativistic molecular model, is a better test. Unfortunately, the authors resorted to a confuse notation and inconsistent equations relating the variables used in their calculation. What is even worse, they did not give any indication of how they determined the adjustable KEP parameter that appears to be the key for obtaining suitable results. We have shown that the simplest MOLCAO calculation with a minimal basis set and an effective nuclear charge is considerably more accurate than the one the authors used for comparison with their KEP. Besides, the variational MOLCAO is completely self consistent while the authors' KEP calculation is based on a parameter adjusted in some unknown way.

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