Comment on: “Solving many-body Schrödinger equations with kinetic energy partition method”, Ann. Phys. 388 (2018) 54-68 by Y-H. Chen and S. D. Chao

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Abstract
We discuss a recent test of the performance of the kinetic energy partition method (KEP) through its application to two separable quantum-mechanical models. We argue that one of the benchmark models is exceedingly simple for testing any realistic approximate method and that almost any reasonable approach yields better results. In the second example our exact benchmark eigenvalues disagree considerably with those chosen by the authors for comparison, which casts doubts on the accuracy of their KEP approach.

Keywords: KEP; coupled oscillators; Harmonium atom; Riccati-Padé method; variational method

1. Introduction
In the last few years a group of authors have been developing the so called “split kinetic energy method” or “kinetic energy partition method” (KEP method from now on)\[1-5\]. This approach is based on splitting the kinetic-
energy part of a nonrelativistic Hamiltonian in order to obtain suitable approximations to the energy levels and corresponding wavefunctions of the Schrödinger equation. In general, the method has been applied to extremely simple nonrealistic models with the exception of the hydrogen-molecule ion in the Born-Oppenheimer approximation \cite{1} and the series of two-electron atoms \cite{4}. The benchmark models are so simple that in some cases \cite{3} they are even completely unsuitable for the chosen physical applications (even for a first-order approximation) \cite{6}.

In the last paper of the series Chen and Chao \cite{5} put forward a generalized version of KEP that may be suitable for the treatment of many-body problems, competing, according to the authors, with well stablised techniques like Hartree-Fock, configuration interaction and density functional theory, among others. In order to illustrate the supposed advantages of KEP they apply it to two separable two-body models, one of which is a trivial textbook example. In this comment we analyze how realistic are such claims.

In section \ref{section1} we discuss a one-dimensional textbook model for a two-electron atom in which the attractive nucleus-electron and repulsive electron-electron interactions are substituted for trivial harmonic potentials. Section \ref{section2} is devoted to the so-called Harmonium atom that is a three-dimensional model where only the nucleus-electron interactions are substituted for harmonic potentials. Finally, in section \ref{section3} we summarize the main results of the paper and draw conclusions.
2. Coupled harmonic oscillators

The first problem is supposed to represent a one-dimensional atom with harmonic instead of Coulomb interactions. It is described by the Schrödinger equation $H\psi = E\psi$ with the Hamiltonian operator

$$H = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) + \frac{k}{2} (x_1^2 + x_2^2) - \frac{K}{2} (x_1 - x_2)^2,$$

(1)

where $x_1$ and $x_2$ are the coordinates of the two electrons of mass $m$ and $k$ and $K$ are the strengths of the nucleus-electron attraction and electron-electron repulsion, respectively [5].

In order to simplify the mathematical treatment of any physical problem it is commonly convenient to resort to dimensionless equations. In the present case we define the dimensionless coordinates $q_i = L^{-1}x_i$, $i = 1, 2$, where $L = \hbar^{1/2}/(mk)^{1/4}$, that lead to the dimensionless Hamiltonian

$$\mathcal{H} = \frac{H}{\hbar\omega} = -\frac{1}{2} \left( \frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial q_2^2} \right) + \frac{1}{2} (q_1^2 + q_2^2) - \frac{\lambda}{2} (q_1 - q_2)^2,$$

(2)

where, $\omega = \sqrt{k/m}$ and $\lambda = K/k$. Note that $E_{jn}(k, K) = \hbar\omega\epsilon_{jn}(\lambda)$, where $E_{jn}$ and $\epsilon_{jn}$ are the eigenvalues of $H$ and $\mathcal{H}$, respectively. The advantage of using a dimensionless equation is not just that it is simpler than the original one (the number of model parameters is reduced to a minimum) but also that we identify the relevant parameters of the system. The common litany “we choose $\hbar = m = 1$” will not do the trick. For example, in this case all the pairs of model parameters $k$ and $K$, treated as different cases by Chen and Chao [5], are basically the same mathematical problem if they have the same ratio $K/k$. 

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This model is a well known textbook example that can be solved exactly. The reason is that the Schrödinger equation is separable by means of the change of variables
\[
\begin{pmatrix}
q_1 \\
q_2
\end{pmatrix} = U \begin{pmatrix}
Q \\
q
\end{pmatrix}, \quad U = \frac{1}{\sqrt{2}} \begin{pmatrix}
1 & 1 \\
1 & -1
\end{pmatrix},
\]
that leads to a sum of two harmonic oscillators:
\[
H = -\frac{1}{2} \left( \frac{\partial^2}{\partial Q^2} + \frac{\partial^2}{\partial q^2} \right) + \frac{1}{2} Q^2 + \left( \frac{1}{2} - \lambda \right) q^2.
\]
Note that this Hamiltonian has bound states only when \( \lambda < 1/2 \), and the corresponding dimensionless eigenvalues are
\[
\epsilon_{jn}(\lambda) = j + \frac{1}{2} + \left( n + \frac{1}{2} \right) \sqrt{1 - 2\lambda}, \quad j, n = 0, 1, \ldots.
\]
If \( \varphi_n^{HO}(k, u) \) is an eigenfunction of the harmonic oscillator \( H^{HO} = -\frac{1}{2} \frac{\partial^2}{\partial u^2} + \frac{k}{2} u^2 \) then the eigenfunctions of \( H \) are of the form \( \psi_{jn}(Q, q) = \varphi_j^{HO}(1, Q) \varphi_n^{HO} \left( \sqrt{1 - 2\lambda}, q \right) \).

As noted above, this model depends essentially on just one parameter \( \lambda \) and several pairs of model parameters chosen by Chen and Chao[5] are basically the same case; for example: \((K, k) = (0.01, 0.02), (0.1, 0.2), (1, 2)\). It is worth noting that they correspond to \( \lambda = 1/2 \) for which the exact wavefunction is not square integrable; however, the KEP solutions derived by those authors appear to be square integrable.

In order to obtain approximate solutions to this exactly solvable problem the authors rewrite the Hamiltonian operator as \( H = K_1 + K_2 \), where \( K_1 = H_1 + H_{12}, K_2 = H_2 + H_{21} \) and
\[
H_i = -\frac{\partial^2}{\partial q_i^2} + \frac{1}{2} q_i^2, \quad i = 1, 2,
\]
Note that these operators are the dimensionless versions (with $\hbar = m = k = 1$, $K = \lambda$) of those chosen by Chen and Chao\cite{5}. The eigenfunctions of $\mathcal{H}$ are written in terms of the eigenfunctions of $H_i$ and $H_{ij}$:

$$H_i \psi_i(q_i) = E_i \psi_i(q_i), \ i = 1, 2,$$

$$H_{ij} \psi_j(\rho) = E_{ij} \psi_{ij}(\rho), \ i \neq j = 1, 2, \ \rho = q_1 - q_2. \quad (7)$$

They first obtain approximate eigenfunctions of $K_i$, $i = 1, 2$ as linear combinations

$$\phi_i(q_i; q_j) = C_i \psi_i(q_i) + C_{ij} \psi_{ij}(\rho), \ i \neq j = 1, 2. \quad (8)$$

Finally, the approximate eigenfunctions are chosen to be

$$\psi(q_1, q_2) = \phi_1(q_1; q_2) \phi_2(q_2; q_1). \quad (9)$$

The authors apply this approach to the ground state and obtain rather complicated expressions with integrals that involve error functions. In our opinion a straightforward Hartree approach, followed by configuration interaction, appears to be simpler and more systematic. However, in what follows we resort to an even simpler approach.

Note that the authors’ approximate wavefunction (9) for the ground state depends on $q_1^2$, $q_2^2$ and $(q_1 - q_2)^2$. Using the same information (and the symmetry of the system) we propose the variational function

$$\varphi^V(q_1, q_2) = \exp \left[ -\alpha \left( q_1^2 + q_2^2 \right) - \beta (q_1 - q_2)^2 \right] , \quad (10)$$
where \( \alpha \) and \( \beta \) are variational parameters. The variational integral is

\[
W(\alpha, \beta) = \frac{\langle \varphi^V | \mathcal{H} | \varphi^V \rangle}{\langle \varphi^V | \varphi^V \rangle} = \frac{4\alpha^3 + 12\alpha^2\beta + \alpha (8\beta^2 - \lambda + 1) + \beta}{4\alpha (\alpha + 2\beta)},
\]

(11)

and the variational conditions \( \partial W/\partial \alpha = 0 \) and \( \partial W/\partial \beta = 0 \) lead to

\[
4\alpha^4 + 16\alpha^3\beta + \alpha^2 \left( 16\beta^2 + \lambda - 1 \right) - 2\alpha\beta - 2\beta^2 = 0,
\]

\[
4\alpha^2 + 16\alpha\beta + 16\beta^2 + 2\lambda - 1 = 0.
\]

(12)

The optimal solution to the latter system of equations is

\[
\alpha_{opt} = \frac{1}{2}, \quad \beta_{opt} = \frac{\sqrt{1 - 2\lambda}}{4} - \frac{1}{4},
\]

(13)

that leads to the exact ground-state energy

\[
W(\alpha_{opt}, \beta_{opt}) = \epsilon_{00}(\lambda) = \frac{1}{2} + \frac{\sqrt{1 - 2\lambda}}{2}.
\]

(14)

Note that we have not resorted to the knowledge of the exact solution in order to build the variational function (10) but to the form of the potential given in (2) or to the form of the KEP function (9). The problem with this trivial example is that most reasonable trial functions will lead to the exact result. In our opinion the KEP approach leads to the most complicated ones and it is unclear how to improve them to obtain better results.

3. Harmonium atom

The second example is somewhat more challenging as it represents two electrons in a space of three dimensions with the Hamiltonian

\[
H = -\frac{\hbar^2}{2m} \left( \nabla_1^2 + \nabla_2^2 \right) + \frac{k}{2} \left( r_1^2 + r_2^2 \right) + e^2 \frac{1}{r_{12}},
\]

(15)
where $m$ and $e$ are the mass and charge of an electron and $k$ is a suitable force constant for the harmonic nucleus-electron attractive part of the potential. As in the preceding example we choose dimensionless coordinates $q_i = L^{-1} r_i$, also with $L = \hbar^{1/2} / (mk)^{1/4}$, and the resulting dimensionless Hamiltonian is

$$\mathcal{H} = \frac{H}{\hbar \omega} = -\frac{1}{2} \left( \nabla_{q_1}^2 + \nabla_{q_2}^2 \right) + \frac{1}{2} \left( q_1^2 + q_2^2 \right) + \frac{\lambda}{q},$$

where $q = |q_1 - q_2| = L^{-1} |r_1 - r_2|$, $\omega = \sqrt{k/m}$ and $\lambda = m^{3/4} e^2 \hbar^{-3/2} k^{-1/4}$.

The Schrödinger equation is separable in terms of the variables

$$Q = \frac{1}{2} (q_1 + q_2), \quad q = q_1 - q_2,$$

that lead to the new Hamiltonian

$$\mathcal{H} = \mathcal{H}_Q + \mathcal{H}_q,$$

$$\mathcal{H}_Q = -\frac{1}{4} \nabla_Q^2 + Q^2, \quad \mathcal{H}_q = -\nabla_q^2 + \frac{1}{4} q^2 + \frac{\lambda}{q}.$$ (18)

The eigenfunctions are of the form $\psi_{\{j\},\{n\}} = f_{\{j\}}(Q) g_{\{n\}}(q)$, where $\{j\}$ and $\{n\}$ are two sets of suitable quantum numbers and $f_{\{j\}}(Q)$ and $g_{\{n\}}(q)$ are eigenfunctions of $\mathcal{H}_Q$ and $\mathcal{H}_q$, respectively. The Schrödinger equation for the three-dimensional isotropic harmonic oscillator $\mathcal{H}_Q$ is exactly solvable and that for $\mathcal{H}_q$ should be solved approximately, except for some particular values of $\lambda$ for which there are exact analytical results (see, for example, reference [11] and the bibliography therein).

In particular, the ground-state eigenvalue is given by

$$E_0 = \hbar \omega \left[ \frac{3}{2} + \epsilon_0(\lambda) \right],$$

where $\epsilon_0(\lambda)$ is the lowest eigenvalue of $\mathcal{H}_q$. As noted above, the advantage of using a dimensionless equation is that we do not have to bother with most
of the physical constants. However, in order to compare present results with those of Chen and Chao\cite{5} we set $\hbar = m = e = 1$ so that equation (19) becomes

$$E_0(k) = \sqrt{k} \left[ \frac{3}{2} + \epsilon_0 \left( k^{-1/4} \right) \right].$$

(20)

We have calculated the eigenvalue $\epsilon_0(\lambda)$ by means of the Riccati-Padé method\cite{8, 9} that converges so fast that yields extremely accurate results\cite{10}. In order to test them we also tried the Rayleigh-Ritz variational method\cite{7} with the unnormalized basis set $f_j = q^j \exp \left( -\frac{q^2}{4} \right), j = 0, 1, \ldots$ (suitable for $s$ states). This approach is known to yield upper bounds to all the eigenvalues\cite{7} (and references therein). Both sets of results agree perfectly and in Table 1 we show the eigenvalue $E_0(k)$ for those values of $k$ chosen by Chen and Chao\cite{5}. Present results and theirs disagree considerably except for the exactly solvable cases $k = 0.25$ ($\lambda = \sqrt{2}$) and $k = 0.01$ ($\lambda = \sqrt{10}$). The two approaches used here yield the exact analytical results in such particular cases: $\epsilon_0 = 5/2$ and $\epsilon_0 = 7/2$, respectively. Figure 1 shows our smooth results and those of Chen and Chao\cite{5} that exhibit a suspicious jagged behaviour.

For this reason and for the fact that our results were obtained by means of two completely different approaches that agree to the last digit we are confident of them. On the other hand, when referring to the “exact” results, Chen and Chao merely point to a paper by other authors\cite{11} (which exhibits just the cases $k = 0.25$ and $k = 0.01$ used for comparison) and do not indicate how the calculation was done. If, as we deem, their benchmark results are inaccurate, then it appears most fortunate that they agree so closely with the KEP ones. Using present exact results as benchmark the errors of the KEP eigenvalues rise considerably for most values of $k$. 
4. Conclusions

The authors promise that they will present an approximate method for the treatment of many-body quantum-mechanical systems that will rival with existing approaches and in the end they merely treat two separable models, one of them exceedingly simple. At first sight this paper appears to be a step backward in the application of KEP to realistic physics problems if one compares it with that earlier work on the ground states of helium-like atoms [4]. There is no doubt that the first model is no suitable benchmark for a realistic approximate method. In the second one the authors apparently failed (that is, of course, our opinion) to obtain accurate results for comparison and one can certainly doubt about the accuracy of their KEP method. In fact, if one takes into account present exact results the KEP errors are considerably larger for some values of $k$.

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Table 1: Eigenvalues of the harmonium atom calculated by means of the Riccati-Padé method

| $k$  | $E_0$                  |
|------|------------------------|
| 0.2500 | 2                      |
| 0.2300 | 1.9273546297410884205  |
| 0.2000 | 1.8116899843671347580  |
| 0.1800 | 1.7292911575097244563  |
| 0.1500 | 1.5958054174355393322  |
| 0.1000 | 1.3360503187251752778  |
| 0.0900 | 1.2760601721269501937  |
| 0.0500 | 0.98925143507101418781 |
| 0.0400 | 0.89879859060929913976 |
| 0.0260 | 0.74778853894031961765 |
| 0.0100 | 0.5                    |
| 0.0040 | 0.34224945694769201625 |
| 0.0013 | 0.21689817637450858280 |
| 0.0012 | 0.21004123606565067787 |
Figure 1: Present ground-state eigenvalues for the harmonium atom (solid line) and those of Chen and Chao\[5\] (dashed line)