Anomaly-free Kohn variational principle

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We show how the Kohn variational principle for the K matrix is free from anomalies when complex short-range basis functions are used. Using only the real part of the K_v matrix increases the accuracy of the calculation and guarantees the unitarity of the resulting S matrix.

INTRODUCTION

The Kohn variational principle[1] (KVP) is a potentially useful method for calculating a K matrix which can then be used to determine a host of scattering parameters (e.g., S matrix, transition probabilities). Kohn's paper derived variational principals for both the S matrix (which we will call the S-KVP) and the K matrix (which we will call the K-KVP). The KVP for the K matrix (K-KVP) has not been widely used due to the presence of the Kohn anomalies.[1(b),2] These are singularities of the variational K matrix (K_v) which occur at energies not associated with resonances in the problem. The position of these anomalies cannot be predicted beforehand. In order to ascertain the reality of a resonance, at least two calculations would have to be carried out. Many researchers since the pioneering work of Schwartz have developed methods for eliminating or reducing the effect of the Kohn anomalies[1(b)] but these introduce complications which limit the practicality of the K-KVP. Recently, several workers[3] have shown that by using a variational principle for the S matrix (S-KVP), instead of the K matrix, the anomalies can be avoided without any further manipulations. It is the purpose of this communication to show how the central idea of the S-KVP can also be used to eliminate the Kohn anomalies in the K-KVP. The K-KVP in this form has a few advantages which may make it more useful than the S matrix version.

The Kohn variational principle for the K matrix is well known and derived in many places.[1] For simplicity sake we will start with a one-channel problem. The variational principle can be written as

$$K_v = \text{ext}\left[K_t - 2\int_0^\infty \psi_t (H-E)\psi_t \, dx\right], \tag{1}$$

where K_t is the trial value of the K matrix and ψ_t is the trial wave function

$$\psi_t \sim v^{-1/2}[\sin(kx) + K_t \cos(kx)], \quad x\to\infty \tag{2}$$

with v the asymptotic velocity and k the asymptotic wave number of the particle. Atomic units are used throughout this paper. The trial wave function is written as

$$\psi_t = u_0(x) + \sum_{i=1}^{n} c_i u_i(x) \tag{3}$$

with $u_0 = v^{-1/2}\sin(kx)$, $u_1 = v^{-1/2} f(x)\cos(kx)$ [$f(0) = 0, f(x) = 1$ as $x\to\infty$ and $u_{i>1}$ short-range basis functions which are zero at the origin and at infinity. The usual variational condition applies, i.e.,

$$\partial K_v/\partial c_i = 0. \tag{4}$$

This yields a set of linear equations for the c_i which can be inverted to yield

$$K_v = -2\left[M_{00} - \sum_{i,j=1}^{n} M_{i0}(\tilde{M}^{-1})_{ij} M_{j0}\right], \tag{5}$$

where

$$M_{kl} = \int_0^\infty u_k (H-E) u_l \, dx,$$
$$\tilde{M}_{kl} = \int_0^\infty u_k (H-E) u_l \, dx, \quad k,l \neq 0. \tag{6}$$

The matrix $\mathbf{M}$ is $(n+1)\times(n+1)$; $\tilde{\mathbf{M}}$ is an $n\times n$ matrix. The basis functions are subject only to the very loose constraints following Eq. (3). Since the K matrix is real, the usual practice is to choose real basis functions suited to a particular problem. The $\tilde{\mathbf{M}}$ matrix is then real symmetric. Its inverse can diverge as the energy is varied. The Kohn anomalies are the divergences which reflect the choice of basis functions and not the real resonances. Increasing the number of basis functions usually decreases the width of the anomalies but at the cost of increasing their number.[1(b),4] Notice, the anomalies are inherent in the procedure and are not due to calculational errors (e.g., the calculation of the overlap integrals).

The central idea in Ref. 3 was to use a variational principle for the S matrix (S-KVP) instead of the K matrix. This variational principle is similar to Eq. (1) and can be written as

$$S_v = \text{ext}\left[S_t + i\int_0^\infty \psi_t (H-E)\psi_t \, dx\right], \tag{1'}$$

where ψ_t is a trial wave function regular at the origin and with the asymptotic form

$$\psi_t \sim -v^{-1/2}[\exp(-ikx) + S_t \exp(ikx)] \tag{2'}$$

with S_t the trial S matrix. The trial wave function can be written as

$$\psi_t = -u_0(x) + \sum_{i=1}^{n} c_i u_i(x) \tag{3'}$$

with $u_0 = v^{-1/2} f(x)\exp(-ikx)$, $u_1 = v^{-1/2} f(x)\exp(ikx)$ [$f(0) = 0$ and $f(x) = 1$ as $x\to\infty$] and $u_{i>1}$ short-range basis functions as before. Applying the variational condition gives

$$S_v = i\left[N_{00} - \sum_{i,j=1}^{n} N_{i0}(\tilde{\mathbf{N}}^{-1})_{ij} N_{j0}\right], \tag{5'}$$

where

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$$N_{kl} = \int_0^\infty u_k (H - E) u_l \, dx,$$

$$\tilde{N}_{kl} = \int_0^\infty u_k (H - E) u_l \, dx, \quad k,l \neq 0. \tag{6'}$$

The wave functions in Eqs. (1') and (6') are *not* complex conjugated. The matrices $\mathbf{N},\tilde{\mathbf{N}}$ are similar to $\mathbf{M},\tilde{\mathbf{M}}$ above. Since $\tilde{\mathbf{N}}$ is *complex symmetric* (not Hermitian) there are no real values of E for which its inverse is singular, i.e., no Kohn anomalies. (The lesson to be learned here is that by using complex basis functions the Kohn anomalies are eliminated in a straightforward manner. We will show how this idea can also be applied to the KVP for the K matrix.) S_v is no longer unitary, but, as more basis functions are used and S_v converges to S_{ex}, S_v also approaches unitarity. The job of inverting the complex matrix $\tilde{\mathbf{N}}$ also becomes a problem as the number of channels and basis functions increase. This can be circumvented by using the standard Löwden–Feshbach partitioning identity in which only real matrices are inverted. (Reference 3 shows how this is done.)

The Kohn anomalies are present even in the simplest scattering problems. To demonstrate this we will calculate K_v for the square well potential (in atomic units)

$$V(x) = \infty, \quad x \leqslant 0,$$
$$= -2, \quad 0 < x \leqslant 1,$$
$$= 0, \quad 1 < x.$$

The wave number $k = 0.8$ a.u. and the mass $m = 1$ a.u. The following basis functions were used in the calculation

$$u_0 = \sin(kx),$$
$$u_1 = [1 - \exp(-Bx)]\cos(kx),$$
$$u_i = x^{i-1}\exp(-Bx), \quad 2 \leqslant i \leqslant 5.$$

To bring out the Kohn anomalies we will vary the parameter B in the basis functions as was done in Ref. 4 instead of the energy, $k^2/2$. The results are plotted in Fig. 1 as $d = (K_v^r/K_{ex}) - 1$ (the superscript r denotes only real basis functions used) as the asterisks vs B. Notice the singularities near $B = 0.8$ and 1.6.

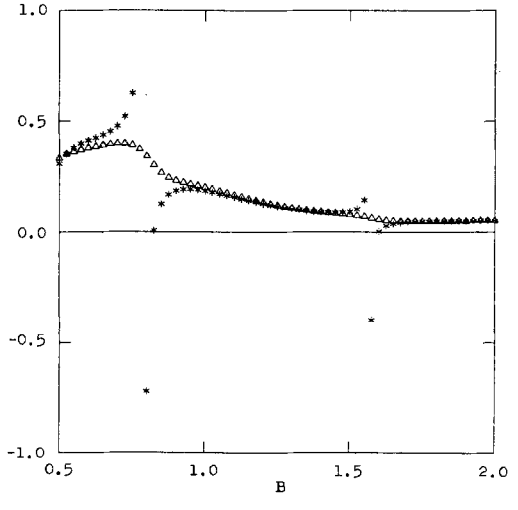

FIG. 1. The real part of $(K_v/K_{ex}) - 1$ vs B for the square well potential described in the text. The asterisks are the results when using purely real short-range basis functions; $u_i = x^{i-1}\exp(-Bx)$, $2 \leqslant i \leqslant 5$. The triangles are the results when u_5 is changed to $u_5 = x^4 \exp[-x(B + 0.1i)]$.

These anomalies are inherent in the variational procedure. However, we have not yet utilized the full flexibility of the KVP for the K matrix. Namely, prior users have restricted themselves to real basis functions. This failure seems to have stemmed from matching the basis functions to the K matrix which is real. But nowhere in the derivation is a condition that the basis functions must be real. If complex basis functions are used, the matrix $\tilde{\mathbf{M}}$ becomes complex symmetric (as in the KVP for the S matrix) and the Kohn anomalies can be pushed off the real line into the complex plane. We have found that a single complex basis function per channel serves to remove the anomalies from the real line. The variational K matrix will be complex symmetric (K_v^c) with the imaginary part of K_v^c automatically small compared to its real part. Since K_{ex} is real symmetric we can eliminate part of the error in K_v^c simply by eliminating its imaginary part. In using only the real part of K_v^c we also regain the unitarity of the S matrix which would be lost if we were to use all of K_v^c. However, $\mathrm{Re}(K_v^c)$ is not variationally stationary. Using only $\mathrm{Re}(K_v^c)$ to calculate the S matrix is simply an intuitive idea which increased the accuracy of all of the calculations described in this paper; its implications have not been studied. In fact, $Im(K_v^c)$ might contain useful information (e.g., on the size of the errors in the calculation), but we do not know how to extract this information (if it exists).

The triangles in Fig. 1 are the results obtained for the square well problem above but with one complex basis function. Specifically, u_5 is changed to $u_5 = x^4 \exp[-x(B + 0.1i)]$. The triangles are $d = \mathrm{Re}[(K_v^c/K_{ex}) - 1]$ (the superscript c denotes the complex basis function used). Notice how the values of d vary smoothly for all B and are nearly indistinguishable from the results of the first calculation away from the singularities. This suggests that by using complex basis functions we improve the accuracy of the calculation only near the anomalies. Note, the functions in Eqs. (1) and (6) are not complex conjugated. To make certain these results were due to the complex nature of u_5 and not to the change of basis functions, we made another calculation using only real functions. We set $u_5 = x^4 \exp(-Bx)\cos(x/10)$ and $u_6 = x^4 \exp(-Bx)\sin(x/10)$. The results are plotted as the circles in Fig. 2. There are now three anomalies, which shows that the lack of singularities in the second calculation was due to the complex nature of u_5.

Both the real and imaginary components of the complex basis function must be linearly independent of all the other basis functions and of each other. If this condition is not satisfied, the K_v^c matrix will have anomalous singularities similar to those when using purely real basis functions. For example, we carried out a calculation in which, instead of u_5, we changed u_2 to $u_2 = x \exp[-x(B + 0.1i)]$; the rest of the basis functions were the same as for the first calculation. The real part of K_v^c was nearly the same as K_v^r of the first calculation because u_2 is very nearly a linear superposition of the other short-range basis functions. The poles of $\tilde{\mathbf{M}}^{-1}$ are too close to the real axis to remove the anomalies. Also, the

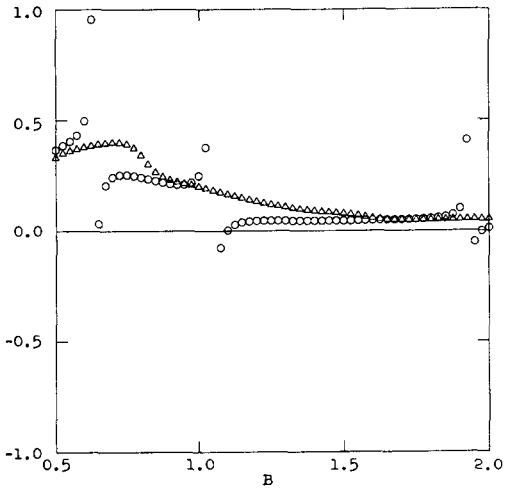

FIG. 2. Same as Fig. 1. The triangles are the same as in Fig. 1. The circles are the results when u_5 is changed to $u_5 = x^4 \exp(-Bx)\cos(x/10)$ and $u_6 = x^4 \exp(-Bx)\sin(x/10)$.

real and imaginary part of the complex basis function should be nearly the same order of magnitude. If the difference between the real and imaginary parts of the complex overlap integrals is too large, the poles of $\tilde{\mathbf{M}}^{-1}$ will again be too close to the real axis to remove the anomalies. For example, using the complex basis function $u = f(x) + i[g(x)/100]$ where $\langle f|f\rangle \simeq \langle g|g\rangle$ would not remove the anomalies.

The similarities between the complex KVP for the K matrix (CK-KVP) and the KVP for the S matrix (S-KVP) include (a) rapidity of convergence to the exact value with increasing number of basis functions. (b) The elimination of Kohn anomalies. (c) The inversion of complex matrices. The CK-KVP has two advantages: (1) part of the error in K_v^c can be analytically eliminated simply by using only its real part. This insures the unitarity of the S matrix which is not the case for the S-KVP. (2) Only one wave function per channel need be complex which means fewer complex matrix elements. The S-KVP has the advantage that the poles of S_v are *automatically* pushed off the real line, while in the CK-KVP this is accomplished only by a careful choice of basis functions.

The similarities between the KVP for the K matrix using complex basis functions (CK-KVP) and the KVP for the S matrix (i.e., using complex boundary conditions) facilitate the transfer of the technology developed by Miller[3] to the CK-KVP (e.g., inverting sparsely complex matrices, calculating exchange integrals). This is especially useful for multichannel problems. The relevant CK-KVP equations for multichannel problems are the same as for the K-KVP (we have not changed the KVP for the K matrix at all, only the assumptions behind its application) so they will not be presented here. We tested the multichannel CK-KVP on the Lester–Bernstein model of an atom-rigid rotor collision.[5] The parameters in Lill, Parker, and Light were used; the K_v matrix was converted into transition probabilities and compared to the "exact" results in their Table II. One complex basis function in each of the nine channels eliminated the Kohn anomalies. Since the recent papers by Miller and coworkers contain multichannel examples and the technology to implement the multichannel CK-KVP, we direct the reader there for details.

In conclusion, the KVP for the K matrix (K-KVP) does not need modification to eliminate the Kohn anomalies; using one complex basis function does the trick. The simplicity of the K-KVP is not lost, and no new technology needs to be developed to implement this procedure, which has the same convergence properties as the KVP for the S matrix and (away from the Kohn anomalies) as the K-KVP and, hence, similar strengths and weaknesses.

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[1](a) W. Kohn, Phys. Rev. **74**, 1763 (1948); (b) R. K. Nesbet, *Variational Methods in Electron-Atom Scattering Theory* (Plenum, New York, 1980), pp. 30–50.
[2]C. Schwartz, Phys. Rev. **124**, 1468 (1961).
[3]W. H. Miller, Comments At. Mol. Phys. **22**, 115 (1988), and references therein; I. C. Percival, Proc. Phys. Soc. **76**, 206 (1960); M. Kanimura, Progr. Theor. Phys. Suppl. **62**, 236 (1977); C. W. McCurdy, T. N. Rescigno, and B. I. Schneider, Phys. Rev. A **36**, 2061 (1987).
[4]K. R. Brownstein and W. A. McKinley, Phys. Rev. **170**, 1255 (1968).
[5]J. V. Lill, G. A. Parker, and J. C. Light, J. Chem. Phys. **85**, 900 (1986); W. A. Lester and R. B. Bernstein, *ibid.* **48**, 4896 (1968).