Variational Estimates using a Discrete Variable Representation

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Abstract

The advantage of using a Discrete Variable Representation (DVR) is that the Hamiltonian of two interacting particles can be constructed in a very simple form. However the DVR Hamiltonian is approximate and, as a consequence, the results cannot be considered as variational ones. We will show that the variational character of the results can be restored by performing a reduced number of integrals. In practice, for a variational description of the lowest $n$ bound states only $n(n+1)/2$ integrals are necessary whereas $D(D+1)/2$ integrals are enough for the scattering states ($D$ is the dimension of the $S$ matrix). Applications of the method to the study of dimers of He, Ne and Ar, for both bound and scattering states, are presented.
1 Introduction

The solution of a quantum mechanical problem can be obtained using a variational principle. It provides second order estimates of binding energies and scattering matrices as well as the corresponding wave functions. For bound states the Rayleigh-Ritz variational principle can be used whereas for scattering states the Kohn variational principle (KVP), among others, can be employed. A common procedure is to combine the variational principle with the expansion of the wave function over a complete basis. Following Ref.[1] we will refer to this method as the variational basis representation (VBR). The accuracy of such a method is strictly connected to the size of the basis set employed. In practical applications the basis set, which in many cases is infinite, is truncated.

For the specific case of bound state calculations the implementation of the VBR method leads to the solution of a generalized eigenvalue problem. The corresponding eigenvalues and eigenvectors represent upper bounds to the exact energy levels of the Hamiltonian and first order approximations to the associated wave functions. If $N$ is the dimension of the truncated basis the Hylleras-Undheim theorem guarantees that

$$E_{\lambda+1}(N) \geq E_{\lambda}(N) \geq E_{\lambda}(N + 1) \ ,$$

(1)

and

$$\lim_{N \to \infty} E_{\lambda}(N) = \epsilon_{\lambda} \ ,$$

(2)

where $\epsilon_{\lambda}$ represents the exact eigenvalue of level $\lambda$. As there is no approximation involved in the calculation of the Hamiltonian matrix elements, the accuracy of the VBR is directly related to the completeness of the basis employed. Accordingly, by increasing the dimension of the basis it is possible to obtain solutions extremely close to the exact ones.

For scattering states the situation is slightly different. The wave function describing a scattering state is not an $L^2$ function, however its form outside the region where the collision takes place is in general known. Therefore the configuration space can be divided into two regions: the asymptotic region in which the particles are either free or interacting through a long range (coulombic) potential, and the internal region. In the asymptotic region the scattering wave function can be described in terms of Bessel or Coulomb functions. In the internal region the scattering state can be expanded over a complete $L^2$-basis. The linear coefficients of the expansion and the $S$ matrix elements giving the relative weights between the ingoing and outgoing asymptotic solutions can be obtained from the KVP. The implementation of
the Kohn variational principle using a VBR leads to a two-step procedure. The first step consists in obtaining a first order estimate of the scattering matrix $S$ and of the wave function by solving a linear non-homogeneous system of equations of dimension $N + D$, with $D$ the dimension of the $S$ matrix. A second order estimate of the $S$ matrix is obtained by inserting the first order solution in the functional:

$$ [S_{\alpha\beta}] = S_{\alpha\beta} + i <\Psi_\beta^-|H - E|\Psi_\alpha^+ >, $$

with $H$ and $E$ the Hamiltonian and the energy of the system respectively. $S_{\alpha\beta}$ is the first order estimate of the corresponding $S$ matrix element and $\Psi_\alpha^+$ ($\Psi_\beta^-$) is the outgoing (ingoing) solution corresponding to channel $\alpha$ ($\beta$). The convergence of the second order estimate of the $S$ matrix elements can be studied for increasing values of $N$. Although in this case there is no guarantee of a monotonous convergence, in contrast with the case for bound states, the properties of the KVP have been extensively studied in past years [2].

The key hypothesis in the variational theorems when implemented with the VBR method is that all the required matrix elements need to be calculated exactly, or at least to a very high accuracy. This means that the computational cost of the calculation increases as $N^2$. It is quite common to choose orthogonal polynomials with appropriate weight functions as basis sets, so that both the norm and the kinetic energy matrix elements are analytical, and the only numerical integrations required are those of the potential matrix elements.

A different, but related technique, is the Discrete Variable Representation (DVR) which is widely used in the description of molecular systems. Examples are the calculations of vibrational spectra, scattering problems or photo-dissociation processes [3, 4]. The DVR method is described in detail in a recent review [5]. The basic property of the DVR is that local operators depending on the inter-particle distance (which include the potential) are diagonal in the DVR basis. However, in the case of the potential matrix the diagonal form is a result of an approximate treatment of the integrals defining the corresponding matrix elements. For example, in the case of an $N$ dimensional basis of orthogonal polynomials multiplied by appropriate weight functions, the approximation consists in replacing the integrals by the related $N$ point Gaussian quadrature formula. In the limit of $N$ going to infinity, both the VBR and the DVR approximations for the energy levels converge to the exact solutions. The advantage of the DVR with respect to the VBR is that there is no need to compute $N^2$ integrals, and the price to
pay is the loss of the variational character of the calculated eigenvalues and eigenvectors.

In the present paper we would like to investigate the possibility of producing variational estimates using the DVR method. For bound states we proceed as follows. The solution of an \( N \) dimensional DVR problem yields \( N \) eigenvalues \( \mathcal{E}^{\text{DVR}}_{\lambda} \) and the corresponding \( N \) eigenvectors \( \psi^{\text{DVR}}_{\lambda} \). The lowest eigenvalue \( \mathcal{E}^{\text{DVR}}_{0} \) is an approximation to the exact ground state \( \mathcal{E}_{0} \). Due to the absence of the variational character, \( \mathcal{E}^{\text{DVR}}_{0} \) could be either greater or smaller than \( \mathcal{E}_{0} \) and this ambiguity remains even for large values of \( N \). However the quantity

\[
\mathcal{E}_{0} = \langle \psi^{\text{DVR}}_{0} | H | \psi^{\text{DVR}}_{0} \rangle
\]

is an upper bound to \( \mathcal{E}_{0} \) provided that the above integral is calculated accurately. To this aim, the \( \psi^{\text{DVR}}_{0} \) wave function, which is known in the DVR basis, that is as amplitudes at the DVR points, has to be transformed to the \( r \)-space. As a result, only one numerical integral needs to be evaluated in order to obtain an upper bound to the ground state energy. As we will see this procedure can be extended to produce upper bounds to the lowest \( n \) levels belonging to a band of the exact Hamiltonian. In this case a minimum of \( n(n + 1)/2 \) integrals have to be computed. In general the number \( N \) of basis functions required to describe correctly the first \( n \) states of an spectral band satisfies \( N >> n \), so that the number of integrals to be performed in order to produce the variational bounds is much smaller than those needed with the VBR. In cases where it is possible to obtain good solutions with \( N \approx n \), the alternatives to the VBR method, such as the one here presented, do not have any particular advantage since the basis functions used to expand the wave functions are already close to the exact solutions.

For scattering states a similar procedure can be followed. If \( S^{\text{DVR}} \) is the first order estimate of the \( S \) matrix element calculated from the KVP using the DVR technique, and \( \psi^{\text{DVR}} \) is the corresponding scattering state, we can use eq. (3) to calculate the second order estimate of the \( S \) matrix element. In order to produce a true variational estimate, the integral of eq. (3) must be calculated accurately. This can be achieved again by transforming the DVR solution to the \( r \)-space. In this manner we have obtained a variational estimate of the \( S \)-matrix elements computing \( D(D + 1)/2 \) numerical integrals, where \( D \) is the dimension of the \( S \)-matrix. In most cases \( D \) is much smaller than the dimension of the basis \( N \).

In order to illustrate the application of the above formalism, we have studied dimers formed by two equal rare gas atoms. The spectrum of small clusters of He, Ne, Ar, Kr and Xe has been the subject of recent investiga-
tions (see Ref. [6] and references therein). In particular, the study of the Helium dimer has proved very challenging, due to the extraordinary features of the He-He interaction that make the He₂ molecule very elusive [7]. Difficulties in the theoretical study of rare gas clusters emerge from the characteristics of the atom-atom interaction, whose attractive part is of the van der Waals type and whose short range part consists of a hard repulsive core, causing those systems to be strongly correlated. As a result, the rotational-vibrational spectrum of these dimers differs substantially from the spectrum of typical covalent or polar molecules. The helium dimer has only one vibrational state, no rotational spectrum and its binding energy is about seven orders of magnitude smaller than that of traditional molecules. Some potential models predict three and nine vibrational states, respectively, for the Ne and Ar dimers however only some of those states have been observed. When the VBR is used to describe the bound states of these dimers a large number of basis functions is required to account for the strong atom-atom correlation. On the other hand the limited number of bound states makes the van der Waals dimers well suited for applications of the method outlined here. We have studied the dimers He₂, Ne₂ and Ar₂ with state-of-the-art atom-atom potentials. In Section II we outline the method as applied to bound states. The convergence patterns of the energies of different states, as well as of other observables, are shown for comparison. In Section III we present results for the scattering lengths and the low energy phase-shifts. Section IV is devoted to the conclusions.

2 Two particles bound states using VBR and DVR

The center of mass Hamiltonian operator for two identical particles is written as

\[ H = -\frac{\hbar^2}{M} \nabla^2 + V(r) \] \hspace{1cm} (5)

where \(M\) is the atomic mass and \(V(r)\) represents the interaction. In order to implement the VBR method we introduce the orthonormal basis \(\Phi_{klm}(r) = \phi_{lk}(r)Y_{lm}(\hat{r})\). The radial basis, which in the following we assume to belong to a family of orthogonal polynomials, satisfies

\[ \int_{0}^{\infty} \phi_{lk}(r)\phi_{lk'}(r)r^2dr = \delta_{kk'} \] \hspace{1cm} (6)

For the sake of clarity, and without loss of generality, we can limit the discussion to \(l = 0\) states and call the corresponding radial basis elements
\( \phi_k (k = 0, 1, \ldots) \). The radial part of the wave function corresponding to the level \( \lambda \) is expanded in terms of the first \( N \) basis elements as

\[
\psi_\lambda(r) = \sum_{k=0}^{N-1} A_\lambda^k \phi_k(r) .
\]  

The linear coefficients \( A_\lambda^k \) and the upper bounds \( E_\lambda \) to the energy levels are obtained from the eigenvalue problem resulting from the Rayleigh-Ritz principle:

\[
\sum_{k' = 0}^{N-1} (H_{kk'} - E_\lambda \delta_{kk'}) A_\lambda^{k'} = 0
\]  

Both the eigenvalues \( E_\lambda \) and the corresponding eigenvectors \( A_\lambda^{k'} \) depend on the size \( N \) of the variational problem solved as is explicitly evident, for instance, from eq. (1). Therefore, a more complete notation would be \( E_\lambda(N) \) and \( A_\lambda^{k'}(N) \). However, in the following we will drop the index \( N \) to simplify the notation.

The Hamiltonian matrix elements \( H_{kk'} \) are the sum of the kinetic and potential energy terms

\[
K_{kk'} = -\frac{\hbar^2}{M} \int_0^\infty \phi_k(r) \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) \phi_{k'}(r) \ r^2 dr ,
\]

\[
V_{kk'} = \int_0^\infty \phi_k(r) V(r) \phi_{k'}(r) \ r^2 dr .
\]

With an appropriate choice of the basis set, the integrals corresponding to the kinetic energy elements \( K_{kk'} \) can be obtained analytically whereas, in general, the integrals corresponding to the potential energy elements \( V_{kk'} \) are calculated numerically. As mentioned in the introduction, the accuracy of the numerical integration must be high enough to prevent error propagation in the computation of the eigenvalues of \( H \). This meets the hypotheses of the variational theorem and assures convergence from above to the exact eigenvalues as the dimension \( N \) of the matrix increases. In the present work the relative accuracy in the computation of the potential energy elements is better than \( 10^{-7} \).

In an alternative approach, the DVR offers a computationally more efficient method for obtaining good estimates of the eigenvalues and eigenvectors of \( H \). Here we briefly introduce the DVR for a basis of \( N \) orthogonal polynomials times the appropriate weight functions \( \Pi \). In this case a one-to-one correspondence exists between the basis representation and the
representation in \( N \) Gaussian quadrature points, however the method is not limited to this case \[1,8\]. The DVR corresponding to the set of \( N \) basis functions \( \phi_k \) can be obtained from the following unitary matrix

\[
T_{k\alpha} = \phi_k(x_\alpha)\sqrt{\omega_\alpha}, \tag{11}
\]

where \( \{x_\alpha\}, \{\omega_\alpha\} (\alpha = 0, \ldots, N - 1) \) are the Gaussian points and weights corresponding to the quadrature formula

\[
\int_0^{\infty} dr r^2 \phi_k(r) V(r) \phi_k'(r) \approx \sum_{\alpha=0}^{N-1} \omega_\alpha \phi_k(x_\alpha) V(x_\alpha) \phi_k'(x_\alpha). \tag{12}
\]

The Gaussian points \( \{x_\alpha\} \) are the DVR points and they can be obtained as the eigenvalues of the \( N \times N \) matrix representation of the coordinate operator \( r \)

\[
r_{kk'} = \int_0^{\infty} dr r^2 \phi_k(r) r \phi_k'(r). \tag{13}
\]

The corresponding eigenvectors form the \( T \) matrix defined in eq. (11).

The right hand side of eq. (12) defines the finite basis representation (FBR) approximation to \( V_{kk'} \) and is called \( V_{k,k'}^{\text{FBR}} \). It corresponds to the computation of the potential matrix elements by quadratures. The potential energy operator in the DVR is defined as

\[
V^{\text{DVR}}_{\alpha\beta} = (T^T V^{\text{FBR}} T)_{\alpha\beta} = V(x_\alpha) \delta_{\alpha\beta}. \tag{14}
\]

The DVR kinetic energy may be expressed as \( K^{\text{DVR}} = T^T K T \), where \( K \) is the matrix whose elements \( K_{kk'} \) are given by eq. (9). Therefore we have introduced two isomorphic representations of \( H \) that have a very simple form. In \( H^{\text{FBR}} = K + V^{\text{FBR}} \), the potential energy matrix has been calculated using an \( N \) point quadrature formula, whereas in \( H^{\text{DVR}} = K^{\text{DVR}} + V^{\text{DVR}} \) the potential energy matrix is diagonal. In both cases the kinetic energy matrix can be obtained analytically \[9\]. The two representations are related by the unitary transformation \( T \), so they have the same set of eigenvalues \( \{E^{\text{FBR}}_\lambda\} = \{E^{\text{DVR}}_\lambda\} \). If \( \psi^{\text{FBR}}_\lambda \) is the eigenvector of \( H^{\text{FBR}} \) with eigenvalue \( E^{\text{FBR}}_\lambda \), then

\[
\psi^{\text{FBR}}_\lambda (r) = \sum_{k=0}^{N-1} B^\lambda_k \phi_k(r) \tag{15}
\]

corresponds to the eigenvector of \( H^{\text{DVR}} \) in \( r \)-space,

\[
\psi^{\text{FBR}}_\lambda (r) \equiv \psi^{\text{DVR}}_\lambda (r) = \sum_{\alpha=0}^{N-1} C^\lambda_\alpha \phi^{\text{DVR}}_\alpha (r). \tag{16}
\]
The coefficients in the above two equations are related to each other by the expression

$$B_k^\lambda = \sum_{\alpha=0}^{N-1} T_{k\alpha} C_{\alpha}^\lambda ,$$  \hspace{1cm} (17)

moreover the DVR basis functions \( \phi_{\alpha}^{\text{DVR}}(r) \) in \( r \)-space are

$$\phi_{\alpha}^{\text{DVR}}(r) = \sum_{k=0}^{N-1} T_{k\alpha} \phi_k(r) \hspace{1cm} (\alpha = 0, \ldots, N - 1).$$  \hspace{1cm} (18)

The \( r \)-space representation of the DVR basis element \( \phi_{\alpha}^{\text{DVR}}(r) \) is a polynomial of degree \( N - 1 \) with zeros at the DVR points \( x_\beta \), with \( \beta \neq \alpha \) [9].

It is important to notice that the linear coefficients \( B_k^\lambda \) in eq. (15) differ from the VBR coefficients \( A_k^\lambda \) of eq. (7) due to the quadrature formula used to calculate the potential energy matrix. As a consequence, the eigenvalues obtained cannot be considered as upper bounds. In fact, we will see that in several cases the energies \( E_{\lambda}^{\text{DVR}} \) oscillate around the convergence value \( \epsilon_\lambda \).

In order to obtain variational estimates, we apply the variational principle to the set \( n \) of DVR eigenvectors \( \psi_{i}^{\text{DVR}}(r) \), \( i = 1, \ldots, n \), which approximate the \( n \) lowest levels of an spectral band of the exact Hamiltonian. In this paper we will discuss the case \( l = 0 \), however the method given below can be applied just as well to other \( l \)-bands. We can build the \( n \times n \) matrix \( \mathcal{H} \) as

$$\mathcal{H}_{ij} = \langle \psi_i^{\text{DVR}} | K + V | \psi_j^{\text{DVR}} \rangle ,$$  \hspace{1cm} (19)

computing the matrix elements of \( V \) numerically using the representation of \( \psi^{\text{DVR}} \) in \( r \)-space. Thus, the computational effort of generating the matrix elements \( \mathcal{H}_{ij} \) is proportional to \( n(n + 1)/2 \). Consequently, the eigenvalues \( \mathcal{E}_{\lambda} \) of \( \mathcal{H}_{ij} \) represent real upper bounds to the eigenvalues \( \epsilon_\lambda \). Moreover, as a consequence of the variational principle, the following relation holds:

$$\epsilon_\lambda \leq E_{\lambda}(N) \leq \mathcal{E}_{\lambda}(n) .$$  \hspace{1cm} (20)

In fact, whereas \( E_{\lambda}(N) \) is the VBR eigenvalue calculated using \( N \) basis functions, \( \mathcal{E}_{\lambda}(n) \) is the eigenvalue calculated using \( n \) specific combinations of the \( N \) basis functions and therefore it is obtained in a reduced Hilbert space. This procedure of generating variational bounds allows for a noticeable gain in computational time with respect to the VBR when the condition \( n << N \) is satisfied. In principle this condition could seem to be a restriction, but in many cases it is valid. For weakly bound molecules, as dimers of rare gases, the number of bound states is not very high. On the other hand, for
systems having a large number of bound states, the number of levels which are approximated well using \( N \) basis functions is generally smaller than \( N \).

In order to illustrate some applications of the above formalism we will calculate the bound states of dimers of He, Ne and Ar. For the He-He and Ne-Ne interactions we use the LM2M2 potential and the HFD-B potential, respectively, both proposed by Aziz and Slaman [10, 11]. For the Ar-Ar system we use the HFD-C potential proposed by Aziz [12]. The values \( \bar{\hbar}^2/M = 43.281307 \), 8.584089 and 4.336093 K a.u.\(^2\) have been used for the He, Ne and Ar systems, respectively. With our choice of the inter-atomic potentials, and of the atomic mass values, the number of vibrational states that result is one for He\(_2\), three for Ne\(_2\), and nine for Ar\(_2\). The corresponding energy values are given in Table I.

For the radial basis functions we have used the following orthonormal basis

\[ \phi_k(r) = \sqrt{\frac{\beta^3}{(k+1)(k+2)}} \mathcal{L}_k^{(2)}(z) e^{-z/2} \]  

where \( \mathcal{L}_k^{(2)} \) is generalized Laguerre polynomial depending on \( z = \beta r \) with \( \beta \) a nonlinear parameter, which can be varied to improve the convergence patterns.

The kinetic terms of eq. (9) have been evaluated using the following analytical form:

\[ K_{kk'} = -\frac{\beta^2 \hbar^2}{M} \left[ \frac{1}{4} (k+1)(k+2) \delta_{kk'} - \frac{1}{3} k^3 - \frac{3}{2} k^2 - \frac{13}{6} k - 1 \right] \quad (k \leq k'). \]  

The non-linear parameter \( \beta \) was chosen to be 1 a.u.\(^{-1}\), 5 a.u.\(^{-1}\) and 10 a.u.\(^{-1}\) for He\(_2\), Ne\(_2\) and Ar\(_2\), respectively.

In figure 1 the convergence of the ground state energy of He\(_2\) is shown as a function of \( N \) for the three methods, VBR, DVR and the mean value calculated using the DVR wave function which in the following has been called \( \langle \text{DVR} \rangle \). It may be observed that the DVR energy \( E_{0}^{\text{DVR}} \) (dashed line) oscillates around the VBR energy \( E_0 \) (solid line) even at very high values of \( N \). The solution becomes stable for \( N > 500 \) revealing the particular structure of the He\(_2\). On the other hand the \( \langle \text{DVR} \rangle \) energy \( \mathcal{E}_0 \) (dotted line) has a much more stable pattern of convergence and already at \( N = 200 \) its value coincides to five digits with the VBR result. In fact, in the figure, the VBR and \( \langle \text{DVR} \rangle \) curves are almost indistinguishable. The \( \langle \text{DVR} \rangle \) calculations can be used to estimate the quality of the DVR wave function. In Table II the total energy, the potential energy and the square root radius are given as functions of \( N \) for the three methods. As already mentioned,
we observe a better stability in the VBR and ⟨DVR⟩ energies. Conversely the DVR and the ⟨DVR⟩ potential energy and square root radius show small differences with respect to the VBR values.

In figure 2 the patterns of convergence of the energy are shown for four selected vibrational states of Ar₂ and Ne₂, as a function of the number N of DVR points. For Ne₂ the HFD-B potential predicts three bound states, however the highest excited state is very loosely bound and has been initially excluded from the analysis. Therefore the wave functions ψ_DVR(λ = 0, 1) have been used to calculate the matrix elements of the Hamiltonian as defined in eq. 19. Accordingly an eigenvalue problem of dimension n = 2 has been solved. For Ar₂ the HFD-C potential predicts nine bound states, but again the highest excited state has been initially excluded, therefore an eigenvalue problem of dimension n = 8 has been solved. We have obtained a good convergence for all the state analyzed for both molecules, but for clarity here we limit the figure to show the energies corresponding to the ground states of the two molecules, the first excited state of Ne₂, and the eighth level of Ar₂. The convergence pattern of these states present some characteristics that merit discussion. As expected the VBR has a very stable convergence in all cases. The DVR energies approach the VBR result with a very fast convergence yielding oscillations of decreasing amplitude as N increases. Though the DVR results are qualitatively similar in the four cases presented, and also in all the other states examined, the ⟨DVR⟩ results for the two ground states have different patterns. Whereas \( E_0 \) for Ne₂ (dotted line in panel (a)) presents a marked oscillatory pattern, \( E_0 \) for Ar₂ (dotted line in panel (c)) presents a convergence extremely close to that of the VBR case. Furthermore, the two ⟨DVR⟩ excited states shown in figure 2 as dotted lines in panels (b) and (d) also present a marked oscillatory pattern. This non monotonic convergence is not in contradiction with the variational principle since the relation presented in eq. 20 holds for each value of N. Moreover these oscillations are a consequence of the non–variational character of the DVR wave functions since in many cases we found that the \( N + 1 \) result is worse than the \( N \) result.

It is possible to improve the convergence of the ⟨DVR⟩ by increasing the number of DVR functions included in the variational problem of eq. 19. If all the N DVR wave functions are included in eq. 19, the VBR and ⟨DVR⟩ methods become isomorphic. Whereas a minimum of \( n \) basis functions is sufficient to produce upper bounds to the \( n \) lowest states of a band, it is reasonable to expect that on increasing the number of functions \( \psi_{\lambda}^{DVR} \) the convergence pattern will improve. Let us call this number \( n' \). In figure 3 the convergence of the two energy levels of Ne₂ (panels (a) and (b)) and
the eighth level of Ar$_2$ (panel (c)) are given as a function of the number $N$
of DVR points, for different sizes $n'$ of the ⟨DVR⟩ problem. We consider the cases $n' = 4, 8, 12$ for Ne$_2$ and $n' = 12, 20, 30$ for Ar$_2$, corresponding to the solid, dashed and dotted-dashed lines, respectively. In all cases the plot of the VBR results is shown as a dotted line. The eighth level of Ar$_2$ represents the most difficult case for the ⟨DVR⟩ method as it requires $n'$ to be consistently larger than $n$ in order to have a smooth convergence pattern. However, we observe that there is a significant improvement in the convergence pattern with choices of $n'$ that still satisfy the important condition $n' \ll N$. Moreover, as expected from the inequality of eq. (20), the $E_\lambda$ energies are always greater than the corresponding $E_\lambda$ energies.

3 scattering states of two particles using VBR and DVR

In order to produce variational estimates for the scattering matrix using the DVR method we use the Kohn variational principle in its general form [2]. Here we give a brief introduction to the method, limiting it to the case of local central potentials. Without loss of generality, we treat specifically the case $l = 0$ and the case in which the collision proceeds along one open channel. In this case the scattering matrix is a scalar quantity. The formalism can be easily generalized to treat more channels and the case in which the long range Coulomb potential is present [13].

The radial scattering wave function corresponding to a process at energy $E$ can be written as a sum of two terms:

$$\psi^+(r) = \psi_c(r) + \psi_\alpha^+(r) .$$

(23)

The first term, $\psi_c$ is the internal part and describes the system when the two particles are close to each other. It can be expanded in terms of $N L^2$ basis functions just as for the bound states

$$\psi_c(r) = \sum_{k=0}^{N-1} A_k \phi_k(r) .$$

(24)

The second term describes a general asymptotic scattering state of two particles and is defined as

$$\psi_\alpha^+(r) = \Omega_0(r) + \mathcal{L}\Omega_1(r) ,$$

(25)
where

\[
\Omega_0 = \sqrt{\frac{Mq}{2\hbar^2}}[u_{00}j_0(qr) + u_{01}\tilde{y}_0(qr)],
\]
\[
\Omega_1 = \sqrt{\frac{Mq}{2\hbar^2}}[u_{10}j_0(qr) + u_{11}\tilde{y}_0(qr)].
\]

are asymptotic scattering states, with \(q^2 = \frac{M}{\hbar^2}E\). They are given as combinations of the regular spherical Bessel function \(j_0\) and the product of the irregular Bessel function \(y_0\) and a regularizing factor, namely

\[
\tilde{y}_0(qr) = (1 - e^{-\gamma r})y_0(qr).
\]

The specific form of the regularizing factor is not crucial provided that the regularization is made in the internal region and \(\tilde{y}_0 \to y_0\) outside the range of the interaction. The quantity \(L\) expresses the relative weight of the two scattering asymptotic states \(\Omega_0\) and \(\Omega_1\). The coefficients \(u_{ij}\) form a matrix that can be chosen in accordance with the different meanings of the quantity \(L\). For example the choices

\[
L = R \quad \text{for} \quad u = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},
\]
\[
L = S \quad \text{for} \quad u = \begin{pmatrix} i & -1 \\ i & 1 \end{pmatrix},
\]

define the reactance matrix \(R\) and the scattering matrix \(S\), respectively.

The generalized KVP states that the functional

\[
[L] = L - \frac{2}{\text{det}(u)} \langle \psi^- | \hat{H} | \psi^+ \rangle
\]

is stationary with respect to variations of the parameters used to construct the wave function. We define \(\hat{H}\) to be \(\hat{H} = (\hat{H} - E)\), \(\text{det}(u)\) is the determinant of the matrix \(u\) and \(\psi^-\) is the complex conjugate of \(\psi^+\). The normalization of the asymptotic states is defined so as to satisfy

\[
\langle \Omega_0 | \hat{H} | \Omega_1 \rangle - \langle \Omega_1 | \hat{H} | \Omega_0 \rangle = \frac{1}{2} \text{det}(u).
\]

The unknowns in the wave function of eq. (23) are the \(N\) linear coefficients \(A_k\) and the quantity \(L\). The variation of the Kohn functional with
respect to these unknowns leads to the following \( N + 1 \) inhomogeneous system of equations

\[
\sum_{k=0}^{N-1} A_k \langle \phi_k | \hat{H} | \phi_{k'} \rangle - \mathcal{L} \langle \phi_{k'} | \hat{H} | \Omega_1 \rangle = -\langle \phi_{k'} | \hat{H} | \Omega_0 \rangle, \quad (k' = 0, \ldots, N - 1),
\]

\[
\sum_{k=0}^{N-1} A_k \langle \phi_k | \hat{H} | \Omega_1 \rangle - \mathcal{L} \langle \Omega_1 | \hat{H} | \Omega_1 \rangle = -\frac{\det(u) + 2 \langle \Omega_1 | \hat{H} | \Omega_0 \rangle + 2 \langle \Omega_0 | \hat{H} | \Omega_1 \rangle}{4}.
\]

The coefficients \( A_k \) as well as the first order estimate of the scattering matrix \( \mathcal{L} \) are obtained from the solution of the above system of equations. The second order estimate \( [\mathcal{L}] \) is calculated substituting the first order solution in eq. (31) and gives

\[
[\mathcal{L}] = \mathcal{L} - \frac{2}{\det(u)} \left\{ \langle \Omega_0 | V | \Omega_0 \rangle + \mathcal{L}^2 \langle \Omega_1 | \hat{H} | \Omega_1 \rangle + \mathcal{L} (\langle \Omega_0 | \hat{H} | \Omega_1 \rangle + \langle \Omega_1 | \hat{H} | \Omega_0 \rangle) \right\}
\]

\[
+ 2\mathcal{L} \sum_{k=0}^{N-1} A_k \langle \phi_k | \hat{H} | \Omega_1 \rangle + 2 \sum_{k=0}^{N-1} A_k \langle \phi_k | \hat{H} | \Omega_0 \rangle \right\}.
\]

The convergence properties of the KVP variational principle have been extensively studied \[14, 15\]. Occasionally singularities occur in its solution, however the complex form (\( \mathcal{L} \equiv S \)) has a much more stable convergence pattern. Here we use both forms and check the consistency of the results by means of the relation

\[
S = (1 + iR)(1 - iR)^{-1}
\]

which holds only for the exact matrices. Moreover the unitary condition for the \( S \) matrix, \( SS^\dagger = I \) is checked as an indication of the completeness of the basis used for the expansion of the internal part of the wavefunction.

The DVR method can be used to calculate the first order estimate of the scattering matrix. For this we write the linear system of eq. (33) in the compact form

\[
\tilde{H} \mathbf{A} = \mathbf{b},
\]

where \( \tilde{H} \) is the \((N + 1) \times (N + 1)\) matrix defined to be \( \tilde{H}_{k,k'} = \langle \phi_k | \hat{H} | \phi_{k'} \rangle \) \((k, k' = 0 \ldots N)\) and writing \( \phi_N \equiv \Omega_1 \). Accordingly, the last element of the vector of coefficients \( \mathbf{A} \) is \( A_N \equiv -\mathcal{L} \) and the elements of the vector \( \mathbf{b} \) are defined to be

\[
b_k = -\langle \phi_k | \hat{H} | \Omega_0 \rangle, \quad k < N,
\]

\[
b_N = -\frac{\det(u) + 2 \langle \Omega_1 | \hat{H} | \Omega_0 \rangle + 2 \langle \Omega_0 | \hat{H} | \Omega_1 \rangle}{4}.
\]
The latter can be reduced to \( b_N = \langle \Omega_0 | \hat{H} | \Omega_1 \rangle \) utilizing eq. (32).

We can now extend the unitary transformation \( T \) which acts in the \( N \times N \) space to the \((N + 1) \times (N + 1)\) space by defining the following unitary matrix \( \tilde{T} \):

\[
\begin{align*}
\tilde{T}_{ij} &= T_{ij} \quad i, j = 0 \ldots N - 1, \\
\tilde{T}_{jN} &= \tilde{T}_{Nj} = 0 \quad j = 0 \ldots N - 1, \\
\tilde{T}_{NN} &= 1.
\end{align*}
\]

(39)

As in the case of the bound state, we first introduce \( \tilde{H}^{\text{FBR}} \) and \( b^{\text{FBR}} \) in which the integrals involving the potential energy operator are calculated using an \( N \) point quadrature formula. The integrals involving the asymptotic functions \( \Omega_p \) are also calculated using quadratures. The corresponding vector of linear coefficients is \( A^{\text{FBR}} \). The DVR representation is defined to be

\[
\tilde{H}^{\text{DVR}} A^{\text{DVR}} = b^{\text{DVR}},
\]

(40)

with

\[
\begin{align*}
\tilde{H}^{\text{DVR}} &= \tilde{T}^t \tilde{H}^{\text{FBR}} \tilde{T}, \\
A^{\text{DVR}} &= \tilde{T}^t A^{\text{FBR}}, \\
b^{\text{DVR}} &= \tilde{T}^t b^{\text{FBR}}.
\end{align*}
\]

(41-43)

The structure of the symmetric matrix \( \tilde{H}^{\text{DVR}} \) is the following

\[
\begin{align*}
\tilde{H}^{\text{DVR}}_{ij} &= K_{ij}^{\text{DVR}} + V(x_i) \delta_{ij} \quad i, j = 0 \ldots N - 1, \\
\tilde{H}^{\text{DVR}}_{Nj} &= \sqrt{w_j} [\hat{H} \Omega_1]_{x_j} \quad j = 0 \ldots N - 1, \\
\tilde{H}^{\text{DVR}}_{NN} &= \sum_{\alpha}^{N-1} w_{\alpha} \Omega_1(x_{\alpha}) [\hat{H} \Omega_1]_{x_{\alpha}}.
\end{align*}
\]

(44-46)

The structure of the inhomogeneous term \( b^{\text{DVR}} \) is

\[
\begin{align*}
b^{\text{DVR}}_j &= -\sqrt{w_j} [\hat{H} \Omega_0]_{x_j} \quad j = 0 \ldots N - 1, \\
b^{\text{DVR}}_N &= -\sum_{\alpha}^{N-1} w_{\alpha} \Omega_0(x_{\alpha}) [\hat{H} \Omega_1]_{x_{\alpha}},
\end{align*}
\]

(47-48)

where \([\hat{H} \Omega_p]_{x_{\alpha}}\) indicates the evaluation of the function \( \hat{H} \Omega_p \) at the DVR point \( x_{\alpha} \). From the above relations we see that only two quadratures have to be performed in order to construct the DVR system of equations. The computational effort is limited as compared to the VBR technique.
The solution $L^{DVR} = -A^{DVR}_N$ represents the DVR first order estimate of the scattering matrix. It coincides with the solution $L^{FBR} = -A^{FBR}_N$ obtained by solving the FBR system. However both differ from the first order scattering $L$, obtained by solving the system of eqs. using the VBR, due to the quadratures introduced to calculate the matrix elements. It is important to notice that the asymptotic integrals $\langle \Omega_1 | \hat{H} | \Omega_1 \rangle$ and $\langle \Omega_0 | \hat{H} | \Omega_1 \rangle$, involved in the construction of the matrix element $\hat{H}^{DVR}_{NN}$ and in the inhomogeneous term $b^{DVR}_N$ respectively, do not depend on the radial basis $\phi_k$ used to expand the scattering wave function. When the VBR technique is used, these integrals are calculated numerically using standard techniques. In the DVR, as it is clear from eqs. and , they depend on the dimension $N$ of the basis. In some cases, the use of the VBR values in $\hat{H}^{DVR}_{NN}$ and $b^{DVR}_N$, instead of those obtained from the quadrature formula, fails to yield the solution (an example will be given at the end of Section III-A). Conversely, the use of the formulas of eqs. and produces a convergence pattern similar to that of the bound states. This means that one has to be very careful in mixing exact integrals and quadratures when using the DVR.

In order to produce a variational estimate of the scattering matrix we construct the DVR radial wave function in $r$-space,

$$\psi^{DVR}(r) = \psi^{DVR}_c(r) + \Omega_0(r) + L^{DVR}_1 \Omega_1(r),$$

where the internal wave function is

$$\psi^{DVR}_c(r) = \sum_{\alpha=0}^{N-1} A^{DVR}_\alpha \phi^{DVR}_\alpha(r).$$

Using eq. and eq. it is possible to calculate the second order estimate of the scattering matrix:

$$[L]^{DVR} = L^{DVR} - \frac{2}{\det(u)} \langle \psi^{DVR} | \hat{H} | \psi^{DVR} \rangle.$$

The integral $\Delta = \langle \psi^{DVR} | \hat{H} | \psi^{DVR} \rangle$ converges since $\hat{H} | \psi^{DVR} \rangle \to 0$ for $r > r_I$, where $r_I$ is the interaction range.

We now consider $[L]^{DVR}$ to be a second order variational estimate of the scattering matrix. It has been obtained calculating one integral, namely the integral $\Delta$. For the case in which $D$ channels are open, $D(D + 1)/2$ integrals must be evaluated. Since, in general, $D \ll N$ the computational effort needed to produce the DVR variational estimate is much smaller than that of the corresponding VBR. In the following subsections we discuss the results for zero and positive energy scattering separately.
3.1 zero energy case

For zero energy scattering the asymptotic wave functions and the KVP assume a particular form. The zero energy wave function is

\[ \psi_0(r) = \psi_c(r) + \psi_a(r), \quad (52) \]

with

\[ \psi_c(r) = \sum_{k=0}^{N-1} A_k \phi_k(r) \quad (53) \]

\[ \psi_a(r) = \Omega_0(r) - a \Omega_1(r). \quad (54) \]

The asymptotic functions are defined to be \( \Omega_0 = \sqrt{M/2\hbar^2} \) and \( \Omega_1 = \sqrt{M/2\hbar^2}(1 - e^{-qr})/r \) and \( a \) is the scattering length. The Kohn functional for the scattering length can be obtained from eq. (31) in which \( L \equiv R \) and taking the limit

\[ \lim_{q \to 0} \frac{\tan \delta}{q} = -a \quad (55) \]

where \( \delta \) is the phase shift and we have used the definition \( R = \tan \delta \). We obtain

\[ [a] = a + 2 \langle \psi_0 | H | \psi_0 \rangle. \quad (56) \]

The minimization of the above functional with respect to the set of coefficients \( \{A_k\} \) and the scattering length \( a \) leads to a linear system of equations formally equal to that of eq. (36) or, in the case of the DVR, to that of eq. (40). We solve both systems to calculate the VBR and DVR first order scattering lengths for the He\(_2\), Ne\(_2\) and Ar\(_2\) systems. As mentioned before, the second order estimates are obtained by substituting the first order solution in eq. (56) calculating the integral \( \langle \psi_0 | H | \psi_0 \rangle \) numerically. Again we use the label \( \langle \text{DVR} \rangle \) for the second order estimate when using the DVR wave function.

In figure 4 (left panel) we show the He-He scattering length (second order) calculated using VBR (solid line) and \( \langle \text{DVR} \rangle \) (dashed line) as a function of the number \( N \) of basis functions. The converged quantity is \( a = 189.518 \) a.u.. The attempt to correct the first order DVR result by calculating the second order estimate using quadratures produces a non-convergent value as is shown in the figure with the dotted line. In the following we call this result DVR\(_q\). To further analyze the differences between the first and second order, in the right panel of figure 4 we show the VBR and DVR first order results. Whereas the first order VBR result converges as the dimension
of the problem increases, the first order DVR result oscillates around the exact value even for \(N > 300\). By comparing the first order DVR result, the DVR\(_q\) result and the \(\langle\text{DVR}\rangle\) result, we conclude that the error introduced by the quadratures in the integral \(\langle\psi_0|H|\psi_0\rangle\) is of the same order of magnitude as the integral itself, therefore it cannot give the correction properly. Conversely, using the DVR as a trial wave function the application of the Kohn functional naturally produces a better approximation. Finally, in figure 5 we show the convergence as a function of \(N\) of the (second order) scattering lengths for the Ne-Ne system (a) and Ar-Ar system (b). The converged values are \(a = 28.411\) a.u. and 520.22 a.u., respectively. The solid, dashed and dotted lines represent the VBR, \(\langle\text{DVR}\rangle\) and the DVR\(_q\) second order estimates, respectively. For Ne the three calculations converge reasonably well. On the contrary, in the case of Ar the VBR presents a fast convergence, the \(\langle\text{DVR}\rangle\) converges after marked oscillations and the DVR\(_q\) fails to converge even for \(N \approx 200\). This is a good example of where the corrective term proportional to \(\Delta\) cannot be calculated using quadratures. The DVR wave functions for the He-He, Ne-Ne and Ar-Ar systems are given in figure 6 corresponding to cases \(N = 300\), \(N = 200\) and \(N = 400\) respectively. Each function presents a number of nodes equal to the number of bound states supported. For the Ar-Ar system a basis of big dimension is needed (\(N = 400\)) in order to produce a wave function orthogonal to the very loosely \(E_8\) state. The values used for the non-linear parameters are \(\beta = 1\) a.u.\(^{-1}\) and \(\gamma = 0.1\) a.u.\(^{-1}\) for He, \(\beta = 5\) a.u.\(^{-1}\) and \(\gamma = 0.1\) a.u.\(^{-1}\) for Ne, and \(\beta = 5\) a.u.\(^{-1}\) and \(\gamma = 0.5\) a.u.\(^{-1}\) for Ar.

Finally we would like to discuss the definition of the elements \(\tilde{H}^{\text{DVR}}_{NN}\) and \(b_{NN}^{\text{DVR}}\) given in eqs. (46) and (48). They correspond to the asymptotic integrals \(\langle\Omega|\hat{H}|\Omega_1\rangle\) and \(\langle\Omega_0|\hat{H}|\Omega_1\rangle\) obtained using quadratures and, because of that, they vary with \(N\). Therefore at each successive step the DVR problem has been solved using different values for those elements. On the other hand, using the VBR, these elements has been computed numerically and independently of \(N\). The differences can be small but significant, for example in some of the present calculations the relative difference between both types of integration is about \(10^{-5}\), for \(N \approx 200\). Analyzing the scattering length convergence pattern as a function of \(N\) using both types of integration we observed small differences in the cases of He and Ar. However the quadrature formula is to be preferred since it provides a first order estimate slightly closer to the final result. In the case of Ne the use of the quadrature formula is mandatory, since otherwise the first order estimates are far from any reasonable value, even for large values of \(N\). This may be understood by comparing the scattering lengths with the interaction range \(r_I\) (estimates
of $r_I$ are given below in B). For He and Ar the scattering length $a$ is much larger than the interaction range whereas this is not the case for Ne. In the latter case there is a delicate cancellation between the internal and the asymptotic part of the wave function in the region $r_I < r < a$. Using DVR this cancellation can be properly achieved only when the definitions of eqs. 46 and 48 are used.

3.2 positive energy case

Here we study the convergence properties of the $l = 0$ phase shift $\delta$ at very low energies using the DVR. In this energy region the phase shift and the scattering length are related by the effective range expansion

$$\frac{q}{\tan \delta} = -\frac{1}{a} + \frac{r_0}{2} q^2 ,$$

(57)

where $r_0$ is the effective range parameter defined to be

$$r_0 = \frac{2}{a^2} \int_0^\infty \left[ (r-a)^2 - \frac{2\hbar^2}{M} (r\psi_0)^2 \right] dr ,$$

(58)

with $\psi_0$ given in eq. (52). Since $(r\psi_0) \to \sqrt{\frac{M}{2\hbar}} (r-a)$ for values of $r > r_I$, the above integral goes very rapidly to zero outside the interaction region. Therefore $r_0$ is itself a measure of the interaction range $r_I$. We obtained the values of 13.94 a.u., 15.65 a.u. and 59.25 a.u. for He, Ne and Ar, respectively.

In Table III we study the convergence of the phase shifts $\delta$ for the He-He and Ne-Ne systems at 50 mK and for the Ar-Ar system at 2 mK. The VBR, DVR$_q$ and $\langle$DVR$\rangle$ results correspond to second order estimates obtained replacing the solutions of the linear systems of eqs. 36,40 in the Kohn functional of eq. 31. Here we do not want to discuss the convergence properties of the KVP, which can be found in Refs. [14, 15]. However, in order to avoid possible singular solutions, we have applied the KVP to the two cases, $L \equiv R$ and $L \equiv S$, and checked the equivalence of the results in accordance with eq. 35. In addition we have verified that on increasing the number of basis functions the quantity $|SS^\dagger - I| \approx 10^{-8}$ in all the cases considered, which is of the same order of magnitude as the differences between the results using $L \equiv R$ or $L \equiv S$. From the table we can see that the DVR$_q$ phase shifts have a slower convergence pattern in all cases. For the He-He system we have seen that at zero energy the DVR$_q$ result is not stable even for large $N$ values. At 50 mK the situation is slightly improved.
though the pattern of convergence of $DVR_q$ is still not satisfactory. For Ne and Ar we observe that big values of $N$ are necessary to obtain stable results. This is due to the presence of excited states close to threshold which are generally difficult to describe, as in the case of the $E_8$ state of Ar.

In figure 7 we compare the quantity $q/\tan \delta$ (filled circles) to the r.h.s of eq. (57) calculated using the zero energy results (solid line). From this plot it is possible to extract the energy at which the phase shift starts to deviate from a linear relation. Below this energy the collision is not very sensitive to the details of the potential since the dynamics is governed by two parameters, the scattering length and the effective range. Greater sensitivity to the potential appears above this energy. For the He system the deviation from linearity starts at about $E = 0.1 \text{ K}$ whereas for Ne it appears at about $E = 0.05 \text{ K}$ and for Ar around $E = 0.002 \text{ K}$.

4 Conclusions

In the present paper we have studied the possibility of using DVR wave functions to produce variational estimates to binding energies and scattering matrices. The main advantage in using the DVR in the description of a quantum mechanical problem is the simplicity in constructing the Hamiltonian matrix. However the DVR eigenvalues do not represent upper bounds to the exact levels. Therefore, in order to obtain estimates to the levels, it is necessary to produce a convergence pattern in terms of the number $N$ of DVR points and analyze the stability of the results as $N$ increases. In the case of the He-He system we have seen that the DVR eigenvalue oscillates around the exact level even for high values of $N$. On the contrary, the variational estimate obtained with the DVR wave function shows a better stability. As a result, calculating only one integral namely the mean value of the Hamiltonian with the DVR ground state wave function, we have improved the prediction using the DVR method.

In order to extend the discussion to excited states, we have studied the Ne-Ne and Ar-Ar systems. We have shown that we need to perform at least $n(n+1)/2$ integrals to produce variational estimates of the first $n$ levels. Although the variational estimates are always upper bounds, we have noticed that, for some levels, they do not converge monotonically, presenting instead oscillations. In order to improve this behavior we have considered a variational problem with an enlarged number ($n'$) of DVR wave functions. We have seen that with $n' \approx 2n$ we obtain convergence patterns very close to those obtained with the VBR. In the case in which the description includes
many excited states with a big spread in energy, we have found it necessary to further increase $n'$. Both $n$ and $n'$ are in general much smaller than $N$, so the possibility of generating variational bounds using the DVR is convenient as compared to the VBR, from the point of view of the computational effort required.

For scattering states the Kohn Variational Principle gives a natural context in which the DVR wave function may be used to calculate second order variational estimates of the scattering matrix. The case of the He-He system at zero energy is a good example. The first order scattering length calculated using DVR oscillates around the exact value. The second order variational estimate calculated using the DVR wave function has a very fast convergence. Conversely, the second order when calculated using quadratures fails to reproduce the correct value for $N < 500$. This is a consequence of the particular structure of the He-He interaction. For the Ne-Ne system the differences between the second order calculated variationally or by using quadratures is not so pronounced as $N$ increases. At the same time, for the Ar-Ar system the second order when calculated using quadratures fails to converge even for values of $N$ of the order of 400. Perhaps this is the best example in which the application of the KVP to correct the first order estimate is clearly necessary. In general we have observed that the scattering calculations need a bigger basis set to obtain converged results. This follows from the fact that the Ne-Ne and the Ar-Ar interactions predict an excited state close to zero energy.

Finally we would like to mention the possibility of extending the present study to the three-body problem. In this case the dimension of the matrices needed for the description of the processes are much bigger. So the capability of producing convergence patterns in terms of $N$ could be limited. Hence variational estimates such as those presented here could help to improve the DVR predictions. A study of this subject is at present in progress.

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Table 1: Spectrum of the He, Ne and Ar dimers calculated with the LM2M2, HFD-B and HFD-C potentials, respectively.

|       | He(mK) | Ne(K)     | Ar(K)     |
|-------|--------|-----------|-----------|
| $E_0$ | -1.3020| -24.4422  | -121.8571 |
| $E_1$ | -4.5281| -84.9229  |           |
| $E_2$ | -0.0327| -55.4794  |           |
| $E_3$ | -33.1574|          |           |
| $E_4$ | -17.4289|          |           |
| $E_5$ | -7.5579 |           |           |
| $E_6$ | -2.3509 |           |           |
| $E_7$ | -0.3409 |           |           |
| $E_8$ | -1.9 $\times 10^{-4}$| | |

Table 2: The He$_2$ binding energy, potential energy and mean square root radius, calculated with the VBR, DVR and $\langle$DVR$\rangle$ methods, as a function of the size $N$ of the basis set employed. Energies are in mK, the radii in a.u.

|       | VBR            | DVR            | $\langle$DVR$\rangle$ |
|-------|----------------|----------------|-----------------------|
| $N$   | $E$            | $V$            | $\sqrt{\langle r^2 \rangle}$ | $E$          | $V$            | $\sqrt{\langle r^2 \rangle}$ | $E$          | $V$            | $\sqrt{\langle r^2 \rangle}$ |
| 50    | -0.0588        | -141.786       | 67.34                 | -0.0742       | -140.622       | 67.65                 | 0.1002       | -140.448       | 67.65                 |
| 100   | -1.2261        | -108.303       | 106.66                | -1.2337       | -108.480       | 106.64                | -1.2177       | -108.464       | 106.64                |
| 150   | -1.2943        | -102.049       | 125.33                | -1.2938       | -102.034       | 125.34                | -1.2942       | -102.035       | 125.34                |
| 200   | -1.3012        | -100.904       | 131.86                | -1.3026       | -100.958       | 131.80                | -1.3012       | -100.957       | 131.80                |
| 250   | -1.3019        | -100.718       | 133.62                | -1.3025       | -100.742       | 133.59                | -1.3019       | -100.742       | 133.59                |
| 300   | -1.3020        | -100.690       | 134.01                | -1.3009       | -100.648       | 134.06                | -1.3020       | -100.649       | 134.06                |
| 350   | -1.3020        | -100.686       | 134.09                | -1.3027       | -100.714       | 134.05                | -1.3020       | -100.713       | 134.05                |
| 400   | -1.3020        | -100.686       | 134.10                | -1.3014       | -100.662       | 134.13                | -1.3020       | -100.662       | 134.13                |
| 450   | -1.3020        | -100.686       | 134.10                | -1.3015       | -100.665       | 134.13                | -1.3020       | -100.665       | 134.13                |
| 500   | -1.3020        | -100.686       | 134.11                | -1.3019       | -100.682       | 134.11                | -1.3020       | -100.682       | 134.11                |
Table 3: Convergence of the second order estimates of the phase shift $\delta$ (in radians) at different energies for the He-He, Ne-Ne and Ar-Ar systems, as a function of the dimension $N$ of the basis. The calculations using the VBR, the DVR$^q$ and the $\langle$DVR$\rangle$ methods are compared.

| $N$ | VBR   | DVR   | $\langle$DVR$\rangle$ |
|-----|-------|-------|------------------------|
|     | He-He (E=50 mK) |       |                        |
| 20  | 1.2563 | -1.3694 | -1.5563                |
| 40  | 1.4685 | 1.4476  | 1.4627                 |
| 60  | 1.4860 | 1.4892  | 1.4741                 |
| 80  | 1.4767 | 1.4635  | 1.4784                 |
| 100 | 1.4883 | 1.4874  | 1.4877                 |
| 120 | 1.4883 | 1.4884  | 1.4882                 |
| 140 | 1.4883 | 1.4879  | 1.4883                 |
| 160 | 1.4883 | 1.4884  | 1.4883                 |
| 180 | 1.4883 | 1.4882  | 1.4883                 |
| 200 | 1.4883 | 1.4884  | 1.4883                 |
|     | Ne-Ne (E=50 mK) |       |                        |
| 20  | 1.0573 | 1.5592  | -1.5708                |
| 40  | 1.3272 | 1.3450  | -0.0693                |
| 60  | 1.3309 | 1.3456  | 1.3209                 |
| 80  | 1.3310 | 1.3311  | 1.3309                 |
| 100 | 1.3310 | 1.3314  | 1.3310                 |
| 120 | 1.3310 | 1.3310  | 1.3310                 |
| 140 | 1.3310 | 1.3310  | 1.3310                 |
|     | Ar-Ar (E=2 mK) |       |                        |
| 10  | 1.2477 | -0.1641 | 1.4324                 |
| 50  | -0.4193 | -0.6421 | -1.5435                |
| 100 | 0.9310 | 1.1382  | -1.4981                |
| 150 | 1.0099 | 1.0077  | 0.9992                 |
| 200 | 1.0109 | 1.0099  | 1.0108                 |
| 250 | 1.0110 | 1.0107  | 1.0111                 |
| 300 | 1.0110 | 1.0108  | 1.0111                 |
| 350 | 1.0110 | 1.0108  | 1.0111                 |
Figure Captions

Figure 1. Ground state energy of He\(_2\), calculated using the VBR (solid line), DVR (dashed line) and ⟨DVR⟩ (dotted line) methods, as a function of the dimension \(N\) of the basis.

Figure 2. (a) ground state energy of Ne\(_2\), (b) first excited state energy of Ne\(_2\), (c) ground state energy of Ar\(_2\) and (d) eighth level of Ar\(_2\), calculated using VBR (solid line), DVR (dashed line) and ⟨DVR⟩ (dotted line), as a function of the dimension \(N\) of the basis. For clarity the results have been drawn with a solid line (VBR), a dashed line (DVR) and a dotted line ⟨DVR⟩.

Figure 3. Convergence patterns for the energy of the ground state of Ne\(_2\) (a), the first excited vibrational state of Ne\(_2\) (b), and the eighth level of Ar\(_2\) (c), for different choices of the size \(n'\) of the restricted variational problem of eq. (19). For Ne\(_2\) the lines correspond to \(n' = 4\) (solid), \(n' = 8\) (dashed) and \(n' = 12\) (dotted-dashed). For Ar\(_2\) the lines correspond to \(n' = 12\) (solid), \(n' = 20\) (dashed) and \(n' = 30\) (dotted-dashed). The VBR results are shown as a dotted line for reference.

Figure 4. Second order estimate for the He-He scattering length \(a\) calculated with the VBR (solid line), ⟨DVR⟩ (dashed line) and DVR\(_q\) (dotted line) as a function of \(N\) (left panel). First order estimate for \(a\), as obtained with the VBR method (solid line), and DVR (dotted line) as a function of \(N\) (right panel).

Figure 5. Second order estimate for the Ne-Ne scattering length \(a\) calculated with the VBR (solid line), ⟨DVR⟩ (dashed line) and DVR\(_q\) (dotted line) as a function of \(N\) (left panel). Second order estimate for the Ar-Ar scattering length \(a\) calculated with the VBR (solid line), ⟨DVR⟩ (dashed line) and DVR\(_q\) (dotted line) as a function of \(N\) (right panel).

Figure 6. Zero energy DVR wave functions for He\(_2\) (upper panel), Ne\(_2\) (middle panel) and Ar\(_2\) (lower panel) calculated using \(N = 300\), \(N = 200\) and \(N = 400\) respectively.

Figure 7. The r.h.s. of eq. (57) (solid line) compared to \(q/\tan\delta\) (filled circles) for He-He (upper panel), Ne-Ne (middle panel) and Ar-Ar (lower panel).
