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A basis for variational calculations in *d* dimensions

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Abstract

In this paper we derive expressions for matrix elements $(\phi_i, H\phi_j)$ for the Hamiltonian $H = -\Delta + \sum_q a(q)r^q$ in $d \geqslant 2$ dimensions. The basis functions in each angular momentum subspace are of the form $\phi_i(r) = r^{i+1+(t-d)/2}\,\mathrm{e}^{-r^p/2}$, $i \geqslant 0$, $p > 0$, $t > 0$. The matrix elements are given in terms of the Gamma function for all d. The significance of the parameters t and p and scale s are discussed. Applications to a variety of potentials are presented, including potentials with singular repulsive terms of the form β/r^α, $\alpha, \beta > 0$, perturbed Coulomb potentials $-D/r + Br + Ar^2$, and potentials with weak repulsive terms, such as $-\gamma r^2 + r^4$, $\gamma > 0$.

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1. Introduction

We study quantum mechanical Hamiltonians $H = -\Delta + V(r)$ in $d \geqslant 2$ dimensions, where V is a spherically symmetric potential that supports discrete eigenvalues, $r = |\mathbf{r}|$, $\mathbf{r} \in \Re^d$. We estimate the spectrum of H in an n-dimensional trial space lying inside an angular-momentum subspace labelled by ℓ and spanned by radial functions with the form

$$\phi(r) = \sum_{i=0}^{n-1} c_i r^{i+1+(t-d)/2}\,\mathrm{e}^{-\frac{1}{2}r^p}, \qquad t > 0. \tag{1.1}$$

If the potential is chosen to be a linear combination of powers

$$V(r) = \sum_q a(q)r^q, \tag{1.2}$$

then all the matrix elements of H may be expressed explicitly in terms of the Gamma function. The expressions obtained will be functions of the parameters t and p, and also of a scale

parameter s to be introduced later. If the potential V is highly singular, the parameter t must be chosen sufficiently large so that $\langle V \rangle$ exists. The advantages of the particular form chosen for the radial functions will become clear in the development. Thus, we have $n+3$ variational parameters with which to optimize upper estimates to the spectrum of H, with one degree of freedom being employed for normalization.

Systems with Hamiltonians of this type have enjoyed wide attention in the literature of quantum mechanics [1–62]. This interest arises particularly from the usefulness of these problems as models in atomic and molecular physics. Many numerical and analytical techniques have been used to tackle Hamiltonians of this form. In section 2 we derive general matrix elements and show how the minimization with respect to scale s can be easily included. In section 3 we discuss some numerical issues not the least of which is the usefulness of the reduction of the matrix eigenequations to symmetric form by first diagonalizing the 'normalization' matrix $N = [(\phi_i, \phi_j)]$. The dependence of the eigenvalues on the parameters $\{p, t, s\}$ may be rather complicated. Since changes to scale s do not involve the recomputation of the basic matrix elements, a policy which emerges is to fix n, always optimize fully with respect to scale s, and, if necessary, optimize approximately with respect to t and p by exploring a few values; if higher accuracy is required, a full optimization is undertaken, or n is increased. In section 4 the matrix elements are applied to a variety of problems and the results are compared with those found in earlier work. We suppose that the Hamiltonian operators in this paper have domains $\mathcal{D}(H) \subset L^2(\Re^d)$, they are bounded below, essentially self-adjoint, and have at least one discrete eigenvalue at the bottom of the spectrum. This, of course, implies that the potential cannot be dominated by repulsive terms. Because the potentials are spherically symmetric, the discrete eigenvalues $E^d_{n\ell}$ can be labelled by two quantum numbers, the total angular momentum $\ell = 0, 1, 2, \ldots$, and a 'radial' quantum number, $n = 1, 2, \ldots$, which counts the eigenvalues in each angular-momentum subspace. These eigenvalues satisfy the relation $E^d_{n\ell} \leqslant E^d_{m\ell}$, $n < m$. With our labelling convention, the eigenvalue $E^d_{n\ell}(q)$ in $d \geqslant 2$ spatial dimensions has degeneracy 1 for $\ell = 0$ and, for $\ell > 0$, the degeneracy is given [63] by the function $\Lambda(d, \ell)$, where

$$\Lambda(d, \ell) = (2\ell + d - 2)(\ell + d - 3)!/\{\ell!(d-2)!\}, \qquad d \geqslant 2, \quad \ell > 0. \tag{1.3}$$

Many techniques have been applied to approximate the spectrum of singular potentials of the form (1.2) using perturbation, variational and geometrical approximation techniques [1–62]. Exact solutions for the energy may be obtained in some special cases by first choosing a wavefunction with parameters, and then finding a potential of the form (1.2) for which this wavefunction is an eigenfunction; this is possible only when certain constraints are satisfied between the parameters $\{a(q)\}$, as we shall discuss later.

2. Matrix elements

We consider first the action of the Laplacian in d dimensions on a wavefunction $\Psi(\mathbf{r}) = \psi(r)Y_\ell(\theta_0, \theta_1, \ldots, \theta_{d-1})$ with a spherically symmetric factor $\psi(r)$ and a generalized spherical harmonic factor Y_ℓ. If we remove the spherical harmonic factor after the action of the Laplacian on Ψ we obtain [64][4]

$$\frac{\Delta\Psi}{Y_\ell} = \psi''(r) + \frac{d-1}{r}\psi'(r) - \frac{\ell(\ell+d-2)}{r^2}\psi(r). \tag{2.1}$$

[4] The Laplacian in N dimensions is discussed on pp 227–231.

The radial Schrödinger equation for a spherically symmetric potential $V(r)$ in d-dimensional space is therefore given by

$$-\frac{\mathrm{d}^2\psi}{\mathrm{d}r^2} - \frac{\mathrm{d}-1}{r}\frac{\mathrm{d}\psi}{\mathrm{d}r} + \frac{l(l+d-2)}{r^2}\psi + V(r)\psi = E\psi, \qquad \psi(r) \in L^2([0,\infty), r^{d-1}\,\mathrm{d}r). \tag{2.2}$$

A correspondence to a problem on the half line in one dimension with a Dirichlet boundary condition at $r = 0$ is obtained with the aid of a radial wavefunction $R(r)$ defined by

$$R(r) = r^{(d-1)/2}\psi(r), \qquad d \geqslant 2, \quad R(0) = 0. \tag{2.3}$$

If we now re-write (2.2) in terms of this new radial function, we obtain the following Schrödinger equation for a problem on the half line:

$$HR = -\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + UR = ER, \qquad R \in L^2([0,\infty), \mathrm{d}r), \tag{2.4}$$

where the effective potential $U(r)$ is given by

$$U(r) = V(r) + \frac{(2\ell+d-1)(2\ell+d-3)}{4r^2}, \tag{2.5}$$

and $H = -\frac{\mathrm{d}^2}{\mathrm{d}r^2} + U$ is the effective Hamiltonian. We note that in (2.5), d and l enter into the equation only in the combination $2l + d$ in $U(r)$: consequently, the solutions for a given central potential $V(r)$ are the same provided $d + 2l$ remains unaltered. In this setting, our trial wavefunctions now have the explicit form

$$R_i(r) = r^{(t+1)/2+i}\exp(-r^p/2) \in L^2([0,\infty), \mathrm{d}r). \tag{2.6}$$

Thus, we have for the general radial function in our trial space

$$R(r) = \sum_{i=0}^{d-1} c_i R_i(r). \tag{2.7}$$

The matrix elements we seek (in a given angular momentum subspace) are given by

$$H_{ij} = (R_i, -R_j'') + \sum_q a(q)(R_i, r^q R_j). \tag{2.8}$$

For each potential term r^q, if we everywhere omit the constant angular factor (equal to 4π in the case $d = 3$), we find the following fomulae, expressed now in terms of the $L^2([0,\infty), \mathrm{d}r)$ inner product:

$$\begin{aligned} P_{ij}(q,p,t) = (R_i, r^q R_j) &= \int_0^\infty r^{i+j+1+t+q}\,\mathrm{e}^{-r^p}\,\mathrm{d}r, \qquad i,j = 0,1,2,\ldots, \\ &= \frac{1}{p}\Gamma\left(\frac{i+j+t+q+2}{p}\right), \qquad t > -(q+2). \end{aligned} \tag{2.9}$$

This type of integral is found by setting $x = r^p$, and using the differential relation $r^k\,\mathrm{d}r = (1/p)x^{(k+1-p)/p}\,\mathrm{d}x$ and the definition of the Gamma function. The normalization integrals are special cases of (2.9), namely

$$N_{ij}(p,t) = (R_i, R_j) = P_{ij}(0,p,t) = \frac{1}{p}\Gamma\left(\frac{i+j+t+2}{p}\right). \tag{2.10}$$

After some algebraic simplifications we find that the corresponding kinetic energy matrix elements $K_{ij}(p,t) = -(R_i, R_j'')$ are given by

$$\begin{aligned} K_{ij}(p,t) = \frac{1}{4p}\Gamma\left(\frac{i+j+t}{p}\right)&[(2\ell+d-1)(2\ell+d-3) \\ &+1-(i-j)^2 + p(i+j+t)], \qquad t > 0. \end{aligned} \tag{2.11}$$

We note that these terms of the Hamiltonian matrix elements H_{ij} are all symmetric under the permutation (ij) (because of Hermiticity), and invariant with respect to changes in d and ℓ that leave the form $2\ell + d$ invariant. These formulae may be used as they stand for all dimensions $d \geqslant 2$ provided that $t > 0$ is chosen sufficiently large $t > -(2 + \hat{q})$ to control the most singular potential term $r^{\hat{q}}$. We note, in addition, that the choice $\{d = 3, \ell = 0\}$ also provides the odd-parity solutions in one dimension.

We now consider the problem of minimizing (R, HR) with respect to the vector v of coefficient $\{c_i\}_{i=0}^{n-1}$ subject to the constraint that $(R, R) = 1$. We immediately obtain the necessary condition:

$$Hv = \mathcal{E}Nv. \tag{2.12}$$

By the min–max characterization of the spectrum [67][5], the eigenvalues of this matrix equation are upper bounds to the unknown exact eigenvalues $E_{i\ell}$, $i = 0, 1, 2, \ldots, n-1$. We assume that these discrete eigenvalues of the underlying operator H are either known to exist, or indeed are demonstrated to exist by the results of this variational estimate. By considering scaled radial wavefunctions of the form

$$R_s(r) = R(r/s), \tag{2.13}$$

we find that factors of s remain only according to the dimensions of the terms. In effect, when using the scaled wavefunctions (2.13), we can leave the matrix N unchanged and replace the matrix for H by

$$H_{ij}(s) = \frac{1}{s^2}K_{ij}(p,t) + \sum_q a(q)s^q P_{ij}(q,p,t). \tag{2.14}$$

Thus, the upper bounds we seek are provided by the eigenvalues of the matrix equation

$$H(s)v = \mathcal{E}Nv, \tag{2.15}$$

which now depend, for a given n and ℓ, on s, p and t and we write

$$E_{i\ell} \leqslant \mathcal{E}_{i\ell} = \mathcal{E}_{i\ell}(p,t,s), \qquad i = 0, 1, 2 \ldots, n-1. \tag{2.16}$$

The problem now is to find these upper estimates and minimize them with respect to the three parameters $\{p, t, s\}$.

3. Some numerical considerations

Rather than solving the general matrix eigenequation (2.7) directly, it is often desirable to use the fact that N is positive definite to transform the problem to symmetric form. In physics literature this is sometimes called a Löwdin transformation [65] and is equivalent analytically to converting the basis functions to an orthonormal set by applying the Gram–Schmidt procedure. We first diagonalize N with the aid of an orthogonal matrix, say S. We then get $S^T NS = M^{-2}$: the square root M exists because N is positive definite, which implies that the diagonal matrix has only positive eigenvalues. The original problem (2.12) (or the scaled version (2.15)) may now be written as

$$Hv = \lambda Nv \rightarrow S^T HSS^T v = \lambda S^T NSS^T v = \lambda M^{-2}S^T v. \tag{3.1}$$

If we multiply on the left by symmetric diagonal matrix M we obtain

$$MS^T HSMM^{-1}S^T v = \lambda M^{-1}S^T v. \tag{3.2}$$

[5] The min–max principle for the discrete spectrum is discussed on p 75 of [67].

If we now write $\mathcal{H} = MS^T HSM$, and $u = M^{-1}S^T v$, we obtain the reduction

$$\mathcal{H}u = \lambda u, \tag{3.3}$$

where $\mathcal{H}^T = \mathcal{H}$. This is the symmetric alternative to our original eigenvalue problem. It has also been shown that the Cholesky decomposition [66] in which the matrix N is written $N = L^T L$, where L is upper triangular, is often numerically faster and more stable than finding the square root M. Computer algebra systems often allow one to solve these problems directly without knowing which method is in fact implemented; the main purpose of our remarks is to show constructively that solutions are always possible.

Another issue is to do with the Gamma function generating large numbers before (or without) the symmetrization of H. To deal with this problem we have found it useful at an early stage to divide all the matrix elements by $(N_{ii}N_{jj})^{\frac{1}{2}}$.

Ideally the matrix eigenvalues should simply be optimized with respect to the parameters $\{p, t, s\}$. In practice this is not always a trivially easy task. Typically, one chooses the basis dimension n and the angular momentum ℓ, and then finds the n eigenvalues. These numbers must be sorted to find, say, the kth eigenvalue $\mathcal{E}_{k\ell}(p, t, s)$, and finally this function must be optimized with respect to the three parameters. This appears to be straightforward until one realizes that the matrix eigenvalue problem must be resolved for each choice of the parameters and, of course, the original ordering can be upset. Logically the kth always has the same numerical meaning but the effect is to make the function $\mathcal{E}_{k\ell}(p, t, s)$ complicated. It is helpful to note that the basic matrices $N(p, t)$, $P(q, p, t)$ and $K(p, t)$ do not depend on s: the Hamiltonian matrix H depends on s by the scaling equation (2.10). In order to reduce the difficulty of the search for a minimum we have sometimes found it useful to fix p and t and to minimize at first only with respect to s; if necessary a graph can be plotted of the dish-shaped function $\mathcal{E}_{k\ell}(s)$ to give a picture of the minimum. This task may then be repeated for some other choices of p and t. In many cases an algorithm such as Nelder–Mead tackles the full minimization problem very effectively and there is no more ado concerning it. We shall make some comments concerning these matters along with the applications described in section 4 below.

4. Applications

We may immediately employ the matrix elements found to solve the eigenvalue problems for the general family of Hamiltonians given by

$$H = -\Delta + \sum_q a(q) r^q. \tag{4.1}$$

One family we shall study in particular is the class of anharmonic singular Hamiltonians

$$H = -\frac{\mathrm{d}^2}{\mathrm{d}r^2} + r^2 + \sum_{q=0}^{N} \frac{\lambda_q}{r^{\alpha_q}}, \qquad r \in [0, \infty) \tag{4.2}$$

where α_q and λ_q are positive real numbers, and we assume that the exact wavefunction ψ of H satisfies a *Dirichlet boundary condition*, namely $\psi(0) = 0$. Inverse power-law potentials $V(r) = \sum_{q=0}^{N} \lambda_q / r^{\alpha_q}$ appear in many areas of physics and for this reason have been widely investigated. The spiked harmonic oscillator Hamiltonian, for example,

$$H(\alpha, \lambda) = -\frac{\mathrm{d}^2}{\mathrm{d}r^2} + r^2 + \frac{\lambda}{r^\alpha}, \qquad \alpha > 0, \quad \lambda > 0 \tag{4.3}$$

has been the subject of many mathematical studies which have greatly improved the understanding of singular perturbation theory [1, 47]. Many different methods [1–62] have been used to study the anharmonic singular Hamiltonians (4.2), such as numerical integration

of the differential equation, perturbative schemes specifically developed for this class of Hamiltonian and variational methods. Among the various methods, the variational method is widely used for calculating energies and wavefunctions since it has the advantage that the eigenvalue approximations are upper bounds [67] (see footnote 5). Many variational techniques used in the literature were designed to solve specific classes of Hamiltonian such as (4.3). Aguilera-Navarro *et al* [31], for example, reported a variational study for the ground-state energy of the spiked harmonic oscillator (4.3) valid only for $\alpha < 3$. Their study makes use of the function space spanned by the exact solutions of the Schrödinger equation for the linear harmonic oscillator Hamiltonian, supplemented by a Dirichlet boundary condition $\psi(0) = 0$, namely, $\psi_n(r) = A_n\, \mathrm{e}^{-r^2/2} H_{2n+1}(r)$, $A_n^{-2} = 4^n(2n+1)!\sqrt{\pi}$, $n = 0, 1, 2, \ldots$ where $H_{2n+1}(r)$ are the Hermite polynomials of odd degree. The matrix elements of the operator $r^{-\alpha}$, $\alpha < 3$, in this orthonormal basis were given as

$$r_{mn}^{-\alpha} = (-1)^{m+n} \frac{\sqrt{(2m+1)!(2n+1)!}}{2^{m+n} m!n!} \frac{\Gamma\left(\frac{3}{2}\right)}{\Gamma\left(n+\frac{3}{2}\right)} \sum_{k=0}^{m} (-1)^k \binom{m}{k} \frac{\Gamma\left(k+\frac{3-\alpha}{2}\right)\Gamma\left(n+\frac{\alpha}{2}-k\right)}{\Gamma\left(k+\frac{3}{2}\right)\Gamma\left(\frac{\alpha}{2}-k\right)},$$
$$\alpha < 3.$$

A variational analysis was carried out and the ground-state upper bounds were reported for the case of $\alpha = 5/2$. Fernandez [53], soon afterwards, designed a particular trial function $\psi(r) = r^{k+1}\, \mathrm{e}^{-\frac{1}{2}sr^{-2}-\frac{1}{2}tr^2}$, $s \geqslant 0, t > 0$, to study the ground state energy of (4.3) for α even integer and for arbitrary value of $\lambda > 0$. An upper bound to the ground state of (4.2) was found by a minimization with respect to $\{s, t\}$ of $E_0(s,t) = ((1-t^2)I_4 + 3tI_2 + 2stI_{-2} - s^2 I_{-4} + \lambda I_{2-\alpha})/I_2$ where $I_n(s,t) = \int_0^\infty r^n \exp(-s/r^2 - tr^2)\, \mathrm{d}t$, $-\infty < n < \infty$. These variational results, however, were not very accurate, even for arbitrary large value of λ owing to the accumulated error in the computation of $I_n(s,t)$. An interesting consequence of Fernandez's work was, however, the exact solution of very particular class of (4.3), namely $H = -\mathrm{d}^2/\mathrm{d}r^2 + r^2 + (9/64)r^{-6}$, where the exact wavefunction in this case reads $\psi(r) = r^{\frac{3}{2}}\, \mathrm{e}^{-\frac{3}{16}r^{-2}-\frac{1}{2}r^2}$ and the exact ground-state energy is $E_0 = 4$. Aguilera-Navarro *et al* [34] afterwards designed another trial function particularly devoted to analyse the ground-state energy of the Hamiltonian $H(4, \lambda)$. A non-orthogonal basis set of trial wavefunctions was introduced by means of $\psi_n(r) = A_n\, {}_1F_1\left(-n; \frac{3}{2}; r^2\right) \exp\left(-ar^2 - \frac{b}{r}\right)$, $n = 0, 1, 2, \ldots$ where A_n is the normalization constant and ${}_1F_1(-n; 3/2; r^2)$ is the confluent hypergeometric function. The expressions for the matrix elements $H_{mn}(4, \lambda)$ were given by

$$H_{mn} = \sum_{q=0}^{n} \sum_{q=0}^{m} \frac{(-n)_p (-m)_q}{\left(\frac{3}{2}\right)_p \left(\frac{3}{2}\right)_q} \frac{A_m A_n}{p!q!} [(4m+3)I(2p+2q+4)$$
$$+ 2\sqrt{\lambda} I(2p+2q+1) - 4q\sqrt{\lambda}(2p+2q-1)]$$

where the definite integrals $I(u) = \int_0^\infty r^u \exp(-r^2 - (2\sqrt{\lambda}/r))\, \mathrm{d}r$ were computed by means of the recursive relations $(u+1)I(u) = (u-1)I(u-2) + 2\sqrt{\lambda} I(u-3)$. The shifted factorial $(a)_n$ is defined by

$$(a)_0 = 1, \qquad (a)_n = a(a+1)(a+2)\cdots(a+n-1), \qquad \text{for} \quad n = 1, 2, 3, \ldots, \tag{4.4}$$

which may be expressed in terms of the Gamma function by $(a)_n = \Gamma(a+n)/\Gamma(a)$, when a is not a negative integer $-m$, and, in these exceptional cases, $(-m)_n = 0$ if $n > m$ and otherwise $(-m)_n = (-1)^n m!/(m-n)!$. The ground state of (4.3) with $\alpha = 4$ then follows by diagonalization of H in the non-orthogonal basis. This particular study was then extended [36] to provide a global analysis of the ground and excited states for the successive values of the orbital angular momentum of the super-singular plus quadratic potential $r^2 + \lambda/r^4$. Another

variational study of the ground state of (4.2) was introduced by Hall *et al* [38] where three-parameter trial functions $\psi(r) = r^{p+\epsilon}\exp(-\beta r^q)$, $p = (\alpha-1)/2$ were used to approximate upper bounds of the ground state of (4.3) for arbitrary α and λ through the minimization of the right-hand side of the inequality $E_0 \leqslant E_0^U$, where

$$E_0^U = \min_{\epsilon,\beta,q>0}\left[\frac{q}{2}(2\beta)^{2/q}\left[(2p+q+2\epsilon-1)g_1 - \frac{2}{q}(p+\epsilon)(p+\epsilon-1)g_2 - \frac{q}{2}g_3\right] + \left(\frac{1}{2\beta}\right)^{2/q} g_4 + \lambda(2\beta)^{\alpha/q} g_5\right] \Big/ g_6$$

and

$$g_1 = \Gamma\left(\frac{2p+2\epsilon+q-1}{q}\right), \quad g_2 = \Gamma\left(\frac{2p+2\epsilon-1}{q}\right), \quad g_3 = \Gamma\left(\frac{2p+2\epsilon+2q-1}{q}\right)$$
$$g_4 = \Gamma\left(\frac{2p+2\epsilon+3}{q}\right), \quad g_5 = \Gamma\left(\frac{2p+2\epsilon-\alpha+1}{q}\right), \quad g_6 = \Gamma\left(\frac{2p+2\epsilon+1}{q}\right).$$

In an attempt to provide a comprehensive variational treatment of the spiked harmonic oscillator Hamiltonian (4.3), for ground-state energy as well for excited states, independent of particular choices of the parameters α and λ, Hall *et al* [40–48] based their variational analysis of the singular Hamiltonian (4.1) on an exact soluble model which itself has a singular potential term. They have suggested and used trial wavefunctions constructed by means of the superposition of the orthonormal functions of the exact solutions of the Gol'dman and Krivchenkov Hamiltonian

$$H_0 = -\frac{\mathrm{d}^2}{\mathrm{d}r^2} + r^2 + \frac{A}{r^2}. \tag{4.5}$$

The Hamiltonian is the generalization of the familiar harmonic oscillator in three-dimension $-\mathrm{d}^2/\mathrm{d}r^2 + r^2 + l(l+1)/r^2$ where the generalization lies in the parameter A ranging over $[0,\infty)$ instead of only values determined by the angular momentum quantum numbers $l = 0, 1, 2, \ldots$. The energy spectrum of the Schrödinger Hamiltonian H_0 is given, in terms of parameter A as

$$E_n = 2(2n+\gamma), \qquad n = 0, 1, 2, \ldots, \tag{4.6}$$

in which $\gamma = 1 + \sqrt{A+\frac{1}{4}}$ and the normalized wavefunctions are

$$\psi_n(r) = (-1)^n\sqrt{\frac{2(\gamma)_n}{n!\Gamma(\gamma)}}r^{\gamma-\frac{1}{2}}\,\mathrm{e}^{-\frac{1}{2}r^2}\,{}_1F_1(-n;\gamma;r^2). \tag{4.7}$$

Here ${}_1F_1$ is the confluent hypergeometric function

$${}_1F_1(-n;b;z) = \sum_{k=0}^{n}\frac{(-n)_k z^k}{(b)_k k!}, \qquad (n\text{-degree polynomial in } z). \tag{4.8}$$

Explicit matrix elements of the Hamiltonian (4.3) can often be found in this orthonormal basis. For instance, the matrix elements of the singular operator $\lambda r^{-\alpha}$ assume the form

$$r_{mn}^{-\alpha} = (-1)^{n+m}\frac{\left(\frac{\alpha}{2}\right)_n}{(\gamma)_n}\frac{\Gamma\left(\gamma-\frac{\alpha}{2}\right)}{\Gamma(\gamma)}\sqrt{\frac{(\gamma)_n(\gamma)_m}{n!m!}}\,{}_3F_2\left(\begin{matrix}-m,\ \gamma-\frac{\alpha}{2},\ 1-\frac{\alpha}{2}\\ \gamma,\ 1-\frac{\alpha}{2}-n\end{matrix}\,\middle|\,1\right), \tag{4.9}$$

where the hypergeometric function ${}_3F_2$ is defined by

$${}_3F_2\left(\begin{matrix}-m,a,b\\ c,d\end{matrix}\,\middle|\,1\right) = \sum_{k=0}^{m}\frac{(-m)_k(a)_k(b)_k}{(c)_k(d)_k k!}, \qquad (m-\text{degree polynomial}).$$

Upper bounds to the energy levels of the Hamiltonian (4.3) then follow by diagonalization of H in the orthonormal basis (4.7). In the case where α is a non-negative even number

Table 1. Upper bounds E^U to the ground-state eigenvalues of $H = -\frac{d^2}{dr^2} + r^2 + \frac{\lambda}{r^\alpha}$ for different values of λ, α. The eigenvalues for the case $\alpha = 2$ are obtained for $n = 1$ and can be compared with the exact formula $2 + \sqrt{1 + 4\lambda}$. The exponent refers to the dimension (n) of the matrix used for the variational computations; the triples in parentheses refer to the approximate initial values of the parameters $\{p, t, s\}$. The small letters indicate references where the same values were obtained in the literature.

λ	$\alpha = 0.5$	$\alpha = 1$	$\alpha = 1.5$	$\alpha = 2$	$\alpha = 2.5$
0.0001	3.000 102$^{(1)a}$	3.000 112$^{(1)a}$	3.000 138$^{(1)a}$	3.000 199 980	3.000 408$^{(14)a}$
	(2.00, 1.00, 1.00)	(2.00, 1.00, 1.00)	(2.00, 1.00, 1.00)	(2.00, 1.00, 1.00)	(2.00, 1.00, 0.79)
0.001	3.001 022$^{(1)d}$	3.001 128$^{(1)b,d}$	3.001 382$^{(1)}$	3.001 998 004	3.004 022$^{(14)c,e}$
	(2.00, 1.00, 1.00)	(2.00, 1.00, 1.00)	(2.00, 1.00, 1.00)	(2.00, 1.00, 1.00)	(2.01, 1.06, 0.78)
0.01	3.010 226$^{(1)}$	3.011 276$^{(1)b,d}$	3.013 794$^{(3)}$	3.019 803 903	3.036 744$^{(15)c,e}$
	(2.00, 1.00, 1.00)	(1.99, 1.00, 0.99)	(1.99, 1.00, 0.99)	(1.99, 1.01, 0.99)	(0.75, 1.56, 0.01)
0.1	3.102 139$^{(3)}$	3.112 067$^{(5)b,d}$	3.135 053$^{(13)}$	3.183 215 957	3.266 874$^{(18)c,e}$
	(2.00, 1.00, 1.00)	(1.90, 1.00, 0.96)	(1.59, 1.00, 0.47)	(2.00, 1.18, 1.00)	(0.57, 1.00, 0.00)
1	3.009 204$^{(13)}$	4.057 877$^{(14)b,d}$	4.141 893$^{(14)}$	4.236 067 978	4.317 311$^{(16)c,e}$
	(2.18, 1.00, 0.98)	(0.99, 1.00, 0.10)	(1.80, 1.06, 0.56)	(2.00, 2.23, 1.00)	(0.69, 1.09, 0.009)
10	12.093 130$^{(14)}$	10.577 483$^{(14)b,d}$	9.324 173$^{(14)}$	8.403 124 237	7.735 111$^{(6)c,e}$
	(1.99, 1.00, 0.9)	(1.00, 1.004, 0.09)	(2.12, 1.69, 1.00)	(1.99, 6.40, 0.99)	(1.70, 5.85, 0.73)

[a] [21]; [b] [33]; [c] [31]; [d] [44]; [e] [41, 59, 29].

$\alpha = 2, 4, 6, \ldots$, the hypergeometric function ${}_3F_2$ in (4.9) can be regarded as a polynomial of degree $\frac{\alpha}{2} - 1$ instead of an m-degree polynomial. Consequently the matrix elements assume much simpler expressions which are useful in numerical computational. For $\alpha \neq 2, 4, 6, \ldots$, the variational computational was then based on direct use of the matrix elements in terms of the hypergeometric function ${}_3F_2$. According to our discussion up to this point, it is clear that most of the variational methods developed in the literature were specifically designed to solve the eigenvalue problem of different classes of the singular Hamiltonian (4.2). No basis set or trial wavefunction were designed to treat a problem such as the singular potentials which at the same time can be used, say, for Hamiltonians with polynomial-type potentials. The purpose of our basis introduced in sections (2) and (3) is to have available at our disposal a working variational approach that can be used without a particular references to specific potentials or special values for the parameters involved. In the following we apply the matrix elements discussed in sections (2) and (3) to solve a number of different eigenvalue problems.

4.1. Spiked harmonic oscillators

We start our applications by investigating the energy levels of the spiked harmonic oscillator Hamiltonian (4.3). As we mentioned in section 3, the problem of finding the eigenvalues reduces to diagonalizing the real symmetric matrix $\mathcal{H} = MS^T HSM$. For $\alpha = 2$, the Hamiltonian (4.3) admits an exact solutions (4.6). Thus it serves as a benchmark for our variational approach. In table 1, we report our upper bounds for the ground state of the spiked harmonic oscillator Hamiltonian (4.3) for several values of the parameters λ and $\alpha = \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}$ along with some results obtained in the literature. For $\alpha = 2$, with $m = n = 0$, table 1 shows that minimization over the three variables $\{p, t, s\}$ yields excellent agreement with the exact solutions (4.6). Such results can be explained by observing that direct substitution of the trial wavefunction $\psi_0(r)$ into the eigenvalue problem

$$H\psi_0 = -\frac{d^2\psi_0}{dr^2} + \left(r^2 + \frac{\lambda}{r^\alpha}\right)\psi_0 = E_0\psi_0 \tag{4.10}$$

Table 2. Comparison of upper bounds for the ground-state energy of the Hamiltonian $H = -\frac{d^2}{dr^2} + r^2 + \frac{\lambda}{r^{5/2}}$ by different variational techniques. The upper bounds E^U are those obtained by this work. The exponent (n) refers to the dimensions of the matrix used for the variational computations.

λ	[31]	[41]	[41]	[38]	E^U
0.001	$3.004\,075^{(30)}$	$3.004\,074^{(30)}$	$3.004\,047^{(5)}$	3.004 04	$3.004\,022^{(14)}$
0.01	$3.039\,409^{(30)}$	$3.039\,244^{(30)}$	$3.037\,474^{(5)}$	3.037 43	$3.036\,744^{(15)}$
0.1	$3.302\,485^{(30)}$	$3.296\,024^{(30)}$	$3.269\,700^{(5)}$	3.269 28	$3.266\,874^{(18)}$
1	$4.329\,449^{(30)}$	$4.323\,263^{(30)}$	$4.318\,963^{(5)}$	4.318 54	$4.317\,311^{(16)}$
10	$7.735\,136^{(30)}$	$7.735\,114^{(30)}$	$7.735\,596^{(5)}$	7.735 32	$7.735\,111^{(8)}$
100	$17.541\,890^{(30)}$	$17.541\,890^{(30)}$	$17.542\,040^{(5)}$	17.541 92	$17.541\,890^{(11)}$
1000	$44.955\,485^{(30)}$	$44.955\,485^{(30)}$	$44.955\,517^{(5)}$	44.955 49	$44.955\,485^{(4)}$

yields for $r \to 0$ that

$$\frac{t^2-1}{4r^2} + \frac{p^2}{4r^{2-2p}} - \frac{(t+1)p}{2r^{2-p}} - \frac{\lambda}{r^\alpha} = 0. \tag{4.11}$$

Consequently, for $\alpha = 2$ and $p > 0$, the value $t = 1 + |1 - \sqrt{1+4\lambda}|$ yields the best possible value of t. As for $\alpha < 2$, similar reasoning yields for $r \to 0$ that $t = 1$ is an excellent *initial* approximation for t, that is to say, suitable for starting the minimization process. In table 2, we present a comparison between different variational approaches for computing upper bounds to the ground state of the Hamiltonian $H = -d^2/dr^2 + r^2 + \lambda r^{-5/2}$ for $\lambda > 0$, where the diagonalization of $\mathcal{H}$, equation (3.3), was carried out in variational spaces of different dimensions n. In table 3, we report our variational computation for upper bounds to the ground-state energy of the Hamiltonian $H = -d^2/dr^2 + r^2 + \lambda r^{-4}$ along with eigenvalues reported in the literature. In table 4, we extended our variational analysis to study the Hamiltonian $H = -d^2/dr^2 + r^2 + l(l+1)/r^2 + \lambda/r^4$ for $\lambda \ll 1$ and for several values of l. We compare our results with those in the literature, along with 'exact' eigenvalues obtained by direct numerical computation of the corresponding Schrödinger equation. In order to keep the number of tables of results to a minimum, we first mention the case of $V(r) = r^2 + \frac{9}{64}\frac{1}{r^6}$ which yields the exact energy $E = 4$: by using our variational approach we obtain an upper bound of $E = 4.000\,0006$ for $n = 15$ with $p = 0.73, t = 7.09$ and $s = 0.01$. The reported results in the tables indicate the general usefulness of matrix elements for the investigation of the entire spectrum of the spiked harmonic oscillator Hamiltonian for $\lambda > 0$ and arbitrary α in any dimensions and for any angular momentum number l. It is also clear that we do not need a very large basis set to produce accurate bounds. It can be seen from the tables that the rate of convergence is fast for moderate values of the coupling constant λ, while for very small values of the coupling constant the rate of convergence is much slower. In general, however, throughout the whole range of values of λ, the result from the introduced basis always gives very reliable upper bounds. In summary, the basis provides a simple, uniform and robust variational method.

4.2. Anharmonic singular Hamiltonian

The anharmonic singular Hamiltonians

$$H = -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + ar^2 + \frac{b}{r^4} + \frac{c}{r^6}, \qquad a > 0, \quad c > 0, \quad l = 0, 1, 2, \ldots \tag{4.12}$$

Table 3. Upper bounds for the ground-state energy E^U for the Hamiltonian $H = -\Delta + r^2 + \frac{\lambda}{r^4}$ for several values of λ. We compare our upper bounds E^U with the literature. The superscript numbers are the dimension of the matrix used; the triples in parentheses refer to the approximate initial values of the parameters $\{p, t, s\}$.

λ	E^U	E
0.0001	$3.022\,275^{22}$	$3.022\,275^{k}$
	(0.30, 3.89, 0.00)	
0.001	$3.068\,763^{20}$	$3.068\,763^{a,c}$, $3.068\,77^{b}$
	(0.33, 8.00, 0.00)	
0.005	$3.148\,352^{20}$	$3.148\,352^{c}$, $3.148\,39^{h}$, $3.148\,35^{g}$
	(0.44, 2.36, 0.001)	$3.146\,64^{d}$, $3.148\,352^{d}$, $3.053\,19^{n}$
		$3.148\,35^{o}$
0.01	$3.205\,069^{20}$	$3.205\,067^{a}$, $3.205\,08^{b}$, $3.204\,42^{d}$
	(0.44, 2.10, 0.00)	$3.205\,07^{k}$, $3.205\,27^{h}$, $3.205\,07^{g}$
		$3.205\,067^{d}$, $3.075\,22^{n}$, $3.237\,75^{k}$
		$3.205\,48^{m}$, $3.205\,07^{o}$, $3.249\,80^{p}$
0.1	$3.575\,559^{14}$	$3.575\,552^{a,c}$, $3.575\,57^{b}$
	(0.42, 9.30, 0.00)	$3.575\,55^{k}$, $3.626\,44^{k}$, $3.600\,44^{p}$
0.4	$4.031\,971^{22}$	$4.031\,971^{i}$, $4.031\,971^{f}$
	(0.50, 3.89, 0.00)	
1	$4.494\,179^{11}$	$4.494\,178^{a}$, $4.494\,18^{b}$
	(0.70, 11.00, 0.00)	$4.494\,18^{k}$, $4.548\,79^{k}$
10	$6.606\,625^{14}$	$6.606\,623^{a,c}$, $6.606\,62^{b}$, $6.606\,62^{k}$
	(0.44, 18.00, 0.00)	$6.649\,78^{k}$, $6.609\,66^{p}$
100	$11.265\,080^{7}$	$11.265\,080^{a}$, $11.265\,08^{b}$, $11.265\,08^{k}$
	(0.49, 72.00, 0.00)	$11.265\,86^{p}$
1000	$21.369\,464^{6}$	$21.369\,463^{a,c,l}$, $21.369\,46^{b}$
	(0.62, 100.80, 0.00)	$21.370\,26^{p}$

[a] [28]; [b] [34]; [c] [28]; [d] [26]; [e] [21]; [f] [29]; [g] [20]; [h] [2]; [i] [8]; [j] [53]; [k] [29]; [l] [20]. [m] [2]; [n] [8]; [o] [44]; [p] [1]; [q] [25]; [s] [38].

Table 4. A comparison between the upper bounds for the Hamiltonian $H = -\frac{d^2}{dr^2} + r^2 + \frac{A}{r^2} + \frac{\lambda}{r^4}$, for a wide range of values of $A = l(l+1)$ and λ, using the present work E^U and the bounds E_a^U obtained by Aguilera-Navarro *et al* [36] (see also [48] and [28]). Accurate numerical results E obtained by direct numerical solution of Schrödinger's equation are also presented. The exponent refers to the dimension (n) of the matrix used for the variational computations; the triples in parentheses refer to the approximate initial values of the parameters $\{p, t, s\}$.

λ	l	E_a^U	E^U	E
0.001	3	9.000 114 279	$9.000\,114\,279^{(11)}$ (1.99, 7.00, 0.99)	9.000 114 279
	4	11.000 063 490	$11.000\,063\,490^{(11)}$ (1.90, 9.00, 1.03)	11.000 063 490
	5	13.000 040 403	$13.000\,040\,403^{(11)}$ (1.98, 9.00, 0.96)	13.000 040 403
0.01	3	9.001 142 268	$9.001\,142\,199^{(11)}$ (2.10, 7.22, 0.98)	9.001 142 199
	4	11.000 634 795	$11.000\,634\,788^{(11)}$ (2.04, 6.91, 1.00)	11.000 634 788
	5	13.000 404 001	$13.000\,404\,000^{(11)}$ (2.01, 7.00, 1.07)	13.000 404 000
0.1	3	9.011 370 328	$9.011\,364\,024^{(13)}$ (2.00, 5.00, 1.19)	9.011 364 024*
	4	11.006 336 739	$11.006\,336\,013^{(13)}$ (2.00, 3.99, 0.84)	11.006 336 013*
	5	13.004 036 546	$13.004\,036\,433^{(8)}$ (1.85, 5.97, 0.79)	13.004 036 433
1	3	9.109 013 250 38	$9.108\,657\,991^{(14)}$ (1.70, 4.00, 0.61)	9.108 657 991*
	4	11.062 293 143 4	$11.062\,241\,722^{(11)}$ (1.90, 8.99, 0.78)	11.062 241 719*
	5	13.040 025 483 8	$13.040\,015\,183^{(8)}$ (1.81, 7.19, 0.77)	13.040 015 183

have attracted considerable attention in part because conditionally exact solutions are possible. From the mathematical point of view, this Hamiltonian is a non-trivial generalization of the spiked harmonic oscillator (4.3). Znojil [7, 8] employed a Laurent series ansatz for the eigenfunctions to convert Schrödinger's equation into a difference equation and then used continued fraction solutions to obtain exact solutions for the ground state and the first excited state. Kaushal and Parashar [68] simplified Znojil's ansatz to obtain exact ground-state expression

$$E_0 = \sqrt{a}\left(4 + \frac{b}{\sqrt{c}}\right) \quad \text{subject to the constraint} \quad (2\sqrt{c} + b)^2 = c(2l+1)^2 + 8c\sqrt{ac}. \tag{4.13}$$

Guardiola and Ros [37] then used a much simpler trial wavefunction $\psi(r) = r^{(b/\sqrt{c}+3)/2}\exp(-r^2/2 - \sqrt{c}/(2r^2))$ for the case of $a = 1$ and $l = 0$ to obtain the exact solution for the ground state as

$$E_0 = 4 + \frac{b}{\sqrt{c}} \quad \text{subject to the constraint condition} \quad (2\sqrt{c} + b)^2 = c + 8c\sqrt{c}. \tag{4.14}$$

For example with $b = c = 1$, the ground state is $E_0 = 5$ and for $b = c = 9$, $E_0 = 7$, etc. Soon afterwards, Landtman [49] performed an accurate numerical calculation and showed that for the parameters chosen by Kaushal and Parashar, although the ground-state energy they obtained agreed with the numerical calculation, their first-excited energy did not. Varshni [51], in an attempt to resolve this problem, obtained four sets of solutions, including one constraint equation for each set and showed that the analytic expression for the energy agrees with the numerical result for any one among the ground, the first- and the second-excited states, depending on the particular constraint condition satisfied. For higher dimensions, by making use of certain ansätze for the eigenfunction, Dong and Ma [52] obtained exact closed-form solutions of (4.12) in two dimensions, where the parameters of the potentials a, b and c again satisfy certain constraints.

In order to compare our variational results with the exact eigenvalues, we have found for the exact ground-state eigenvalue $E_0 = 5$ of the Hamiltonian (4.12) with $l = 0$, $a = b = c = 1$, an upper bound of $E_0 = 5.000\,006$ obtained by the diagonalization of a 14×14 matrix. Further, the exact energies of $7, 7, 11, 11$ corresponding to $(a, b, c) = (1, 9, 9), (1, -7, 49), (1, 45, 225)$ and $(1, -24.5125, 600.8623)$ respectively, follow by the optimization of the matrix eigenvalues with initial guesses for the variational parameters and matrix dimensions given respectively, by $(p, t, s) = (1.12, 16.09, 0.11), (1.03, 27.47, 0.07), (1.10, 31.00, 0.10)$, and $(0.77, 40.82, 0.01)$, and $14 \times 14, 11 \times 11, 8 \times 8$ and 7×7. These results indicate the generality and the efficiency of our approach. Note $(b, c) = (-7, 49)$, and $(b, c) = (-24.5125, 600.8623)$ also shows the applicability of the method in the case of b negative. We further illustrate the applicability of the matrix elements to obtain accurate upper bounds to the ground state of (4.12) for several values of a, b and c. Indeed, for $(a, b, c) = (1, 10, 1), (1, 10, 10)$, and $(1, 100, 100)$, we obtain $6.679\,053, 7.138\,261$, and $11.791\,771$ respectively, whose results are in excellent agreement with the exact eigenvalues obtained by direct numerical integration of Schrödinger's equation. The precision of the upper bounds to any number of decimal places can be achieved by increasing n, the dimension of the matrix. The energies of the excited states in arbitrary spatial dimension d are similarly straightforward to find.

4.3. Perturbed Coulomb potentials

Hautot [60], in his solutions of Dirac's equation in the presence of a magnetic field, introduced some interesting methods of solving certain second-order differential equations. One of these methods deals with the potential operator

$$V(r) = -D/r + Br + Ar^2, \qquad A \neq 0. \tag{4.15}$$

Hautot obtained exact solutions for only certain relations between the constants A, B and D. He achieved his results by applying the kinetic energy operator to an appropriate wavefunction and using the standard procedure of comparing coefficients in the induced recurrence relations. More precisely, by introducing [39]

$$\psi(r) = \exp\left(-\frac{1}{2}\left(\sqrt{A}r^2 + \frac{Br}{\sqrt{A}}\right)\right)\sum_{k=0}^{n} a_k r^{k+l}, \qquad n = 0, 1, 2, \ldots$$

into the radial Schrödinger equation

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r} - \frac{l(l+1)}{r^2} + E + \frac{D}{r} - Br - Ar^2\right)\psi(r) = 0.$$

One obtains the following three-term recursion relation between the coefficients a_k for $(k = 0, 1, 2, \ldots)$:

$$[(k+2)(k+2l+3)]a_{k+2} + \left[D - \frac{B}{\sqrt{A}}(k+2+l)\right]a_{k+1} + \left[E - \sqrt{A}(2k+2l+3) + \frac{B^2}{4A}\right]a_k = 0.$$

This recurrence relation terminates if $a_{k+1} = 0$, that is to say $E = E_{nl} = \sqrt{A}(2n+2l+3) - \frac{B^2}{4A}$ provided that the parameters A, B and D satisfy the $(n+1) \times (n+1)$-determinant

$$\det\begin{pmatrix} a_0 & b_0 & & & & & & \\ c_1 & a_1 & b_1 & & & & & \\ & c_2 & a_2 & b_2 & & & & \\ & & \cdot & \cdot & \cdot & \cdot & & \\ & & & \cdot & \cdot & c_{n-1} & a_{n-1} & b_{n-1} \\ & & & & & & c_n & a_n \end{pmatrix} = 0, \qquad \text{where}$$

$$\begin{cases} a_k = D - \frac{B}{\sqrt{A}}(k+l+1), \\ b_k = (k+1)(k+2l+2), \\ c_k = E_{nl} - \sqrt{A}(2k+2l+1) + \frac{B}{\sqrt{A}}. \end{cases}$$

For example, we have for the ground-state energy (i.e. $k, l = 0$) of

$$V(r) = -\frac{1}{r} + Ar + (Ar)^2, \qquad E_0 = (3+2l)A - \frac{1}{4}, \tag{4.16}$$

with the ground-state wavefunction given explicitly as $\psi(r) = r^l \exp\left(-\frac{1}{2}(r + Ar^2)\right)$. This particular case was studied by Killingbeck [17] who obtained the exact solution for the ground state for $\beta > 0$. In order to test the variational approach discussed in sections 2 and 3, we have employed the matrix elements to obtain upper bounds to the exactly solvable cases such as $\beta = 0.1$, 1, and 2, we found that the upper bounds yield 0.05, 2.75 and 5.75 which are in excellent agreement with the exact eigenvalues as given by (4.16). An important consequence of our variational approach is the upper bounds that are easily obtained for unconstrained values of D, B and A. In table 5, we have reported our variational results for $D = 1$ and

Table 5. Upper bounds for the Hamiltonian $H = -\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{D}{r} + Br + Ar^2$ for different values of the parameters B and A. The numerical results in the brackets are the exact eigenvalues as obtained by direct numerical integration of Schrödinger equation. The triples in parentheses refer to the approximate initial values of the parameters $\{p, t, s\}$.

D	B	A	E^U
1	1	2	3.656 525 (3.657)
			8×8, (1.99, 1.00, 0.73)
1	0.1	1	1.885 424 (1.885)
			11×11, (1.92, 1.00, 0.75)
1	0.5	1	2.277 581 (2.278)
			10×10, (2.04, 1.00, 0.86)
1	0.1	0.1	0.378 305 (0.378)
			12×12, (2.21, 1.00, 1.63)
1	0.01	1	1.795 268 (1.795)
			8×8, (1.08, 1.00, 0.09)
1	0.001	1	1.786 212 (1.786)
			8×8, (2.04, 1.00, 0.93)

Table 6. Comparison of the eigenvalues for $H = -\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{D}{r} + Br + Ar^2$ for different values of D, B and A where E^N is calculated from the shifted $1/N$ expansion [30], the exact supersymmetric values E^s [30] and the upper bounds E^U obtained by the method of this paper (diagonalization of the $n \times n$ matrix elements then minimizing with respect to the parameters $\{p, t, s\}^n$).

l	D	B	A	E^N	E^s	E^U
0	1	0.447 21	0.1	0.171 66	0.170 82	$0.170\,82^6$
1	1	0.223 61	0.1	0.993 37	0.993 03	$0.993\,04^8$
2	1	0.149 07	0.1	1.509 79	1.509 69	$1.509\,69^3$
3	1	0.111 80	0.1	1.981 24	1.981 21	$1.981\,21^3$
0	1	1.414 21	1.0	1.627 56	1.621 32	$1.621\,32^4$
1	1	0.707 11	1.0	3.411 41	3.410 53	$4.410\,54^8$
2	1	0.471 40	1.0	4.894 40	4.894 19	$4.894\,19^4$
3	1	0.353 55	1.0	6.332 78	6.332 71	$6.332\,71^1$
0	1	4.472 14	10	6.226 80	6.208 20	$6.208\,22^4$
1	1	2.236 07	10	11.057 19	11.055 34	$11.055\,34^2$
2	1	1.490 71	10	15.597 32	15.596 92	$15.596\,92^4$
3	1	1.118 03	10	20.093 49	20.093 36	$20.093\,37^{10}$
0	1	14.142 14	100	20.753 21	20.713 20	$20.713\,20^4$
1	1	7.071 07	100	35.233 90	35.230 34	$35.230\,34^5$
2	1	4.714 05	100	49.442 67	49.441 92	$49.441\,92^9$
3	1	3.535 53	100	63.608 60	63.608 36	$63.608\,37^8$
0	1	44.721 36	1000	66.659 04	66.582 04	$66.582\,04^3$
1	1	22.360 68	1000	111.685 01	111.678 40	$111.678\,40^7$
2	1	14.907 12	1000	156.470 58	156.469 20	$156.469\,20^7$
3	1	11.180 34	1000	201.215 30	201.214 87	$201.214\,87^7$

several values of B and A where we compare our results with the upper bounds obtained by the direct numerical integration of Schrödinger's equation [39]. In arbitrary dimensions, the matrix elements discussed in sections 2 and 3 provide a uniformly simple, straightforward and efficient way of obtaining accurate energy bounds for the entire spectrum. In order to compare our results with those in the literature, we consider in table 6 the radial Schrödinger equation

Table 7. Upper bounds for the Hamiltonian $H = -\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \gamma r^2 + r^4$ with different values of γ. $E_1(V)$ and $E_3(V)$ represent the values obtained from the variational method discussed by Broges *et al*, and E_1^U and E_3^U are from this work (with a 10×10 matrix). We have also included accurate numerical results E_1^N and E_3^N obtained by direct numerical integration of Schrödinger's equation.

γ	$E_1(V)$	E_1^N	E_1^U	$E_3(V)$	E_3^N	E_3^U
0.1	3.710 64	3.708 93	3.708 93	11.542 58	11.488 48	11.488 48
0.2	3.618 90	3.617 01	3.617 01	11.386 92	11.331 27	11.331 27
0.3	3.525 96	3.523 87	3.523 87	11.230 45	11.173 10	11.173 10
0.4	3.431 79	3.429 47	3.429 47	11.073 07	11.013 97	11.013 97
0.5	3.336 36	3.333 78	3.333 78	10.914 77	10.853 87	10.853 87
0.6	3.239 62	3.236 76	3.236 76	10.755 56	10.692 80	10.692 80
0.7	3.141 55	3.138 37	3.138 37	11.595 47	10.530 74	10.530 74
0.8	3.042 10	3.038 56	3.038 56	10.434 48	10.367 70	10.367 70
0.9	2.941 23	2.937 30	2.937 30	10.272 58	10.203 67	10.203 67
1.0	2.838 91	2.834 54	2.834 54	10.109 78	10.038 65	10.038 65
2.0	1.726 29	1.713 03	1.713 03	8.433 95	8.332 87	8.332 87

in d-dimensions in the form

$$-\frac{1}{2}\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\Lambda(\Lambda+1)}{r^2}\right)\psi + \left(-\frac{a}{r} + br + cr^2\right)\psi = E\psi \tag{4.17}$$

where $\Lambda = (d + 2\ell - 3)/2$. The overall factor of $1/2$ in the kinetic energy was incorporated in our calculations by multiplying the kinetic energy matrix elements (2.11) by this quantity. To analyse the precision of the method, we again compare our results in table 6 with some special cases for which the eigenvalues are known [30]. Results for the excited states within each angular momentum subspace (labelled by ℓ) are automatically provided for (up to the dimension of the matrix used), and arbitrary spatial dimension d is allowed for in the general expressions for the matrix elements.

4.4. The quartic double-well potential $V(r) = -\gamma r^2 + r^4$, $\gamma > 0$

The quartic double-well potential

$$V(r) = -\gamma r^2 + r^4, \qquad \gamma > 0, \tag{4.18}$$

has a long history of numerical studies (see, for example, [61, 62] and the references therein). Apart from its intrinsic interest, the double-well potential also plays an important role in the quantum study of the tunnelling time problem [69], in spectra of molecules such as ammonia and hydrogen-bonded solids [70]. Broges *et al* [71], using supersymmetry techniques, constructed trial wavefunctions for variational calculations of the ground state, first-, second- and third-excited-states. In their comparison with the literature, they have used the results obtained from direct numerical integration of the corresponding Schrödinger equation, as reported in [72]. Unfortunately, these numerical eigenvalues were not very accurate and the errors are higher than what appear in their reported tables. In table 7, we compare our results for the first- and third-excited states with those of Broges *et al* [71], who considered the problem in one dimension; we also include accurate numerical values.

5. Conclusion

We have found matrix elements for Schrödinger operators in d spatial dimensions with spherically symmetric potentials of the form $V(r) = \sum_q a(q)r^q$. The matrix elements for a

given angular momentum ℓ are calculated with respect to a finite basis $\{\phi_i\}_{i=0}^{n-1}$ comprising polynomials in r with an overall factor of the form $r^{1+(t-d)/2}\,\mathrm{e}^{-r^p/2}$. With the inclusion of a scale parameter s, the upper estimates are the eigenvalues $\mathcal{E}_i^{[n]}(p,t,s)$ of an $n \times n$ matrix eigenequation of the form $Hv = \lambda Nv$, where $N = [(\phi_i, \phi_j)]$. For best results, these estimates are optimized with respect to the three parameters $\{p, t, s\}$ for a given n. For the class of problems considered, the basis has the advantage that explicit analytic expressions in terms of the Gamma function are available for all the matrix elements. The method is robust and flexible enough to yield excellent results for the whole class of problems without the need to work with very large matrices.

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