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On the long-range and short-range behavior of potentials from reproducing kernel Hilbert space interpolation

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The long-range behavior of potential energy functions is important in many areas of physics. For example, the long-range forces between atoms and molecules are crucial in understanding low-energy collisions[1] and the properties of complexes near dissociation.[2] Ultra-low-energy collisions are particularly topical because of recent experiments involving atoms and ions in traps, and there is great interest in the properties of ultracold molecules produced either by buffer-gas cooling[3] or by photoassociation of atoms in a Bose condensate.[4] Properties such as scattering lengths and densities of states near dissociation can be strongly influenced by the potential at very long range. It is thus quite important to use potential energy functions that have the correct asymptotic behavior.

An increasingly popular approach to generating potential energy functions is to carry out *ab initio* or other calculations on a grid of points and then interpolate between them and extrapolate beyond them. Many procedures are available for this. A particularly attractive interpolation method is the reciprocal power reproducing kernel Hilbert space (RP-RKHS) approach,[5,6] which was formulated specifically for molecular potential energy surfaces. However, the RP-RKHS method was not designed for extrapolation at short range, and considerable inaccuracies can result if it is used in that way.

The aim of this Note is to analyze the asymptotic properties of radial functions obtained from RP-RKHS interpolation and to obtain explicit formulae for their behavior when used to extrapolate at short and long range. The results illustrate both the power of the method at long range and the dangers of misusing it to extrapolate at short range. We discuss in detail only the one-dimensional case, but the generalization to multi-dimensional cases is straightforward.

For a set of points $\mathcal{V}(r_i)$, where $i=1,2,\ldots,p$ and $r_1 < r_2 < \cdots < r_p$, a family of interpolating RP-RKHS potential functions $V^{[n,m]}$ is defined by

$$V^{[n,m]}(r)=\sum_{i=1}^{p} \alpha_i^{[n,m]} q^{[n,m]}(r,r_i) \tag{1}$$

and

$$q^{[n,m]}(x,x')=\frac{1}{x_>^{m+1}} \sum_{k=0}^{n-1} \beta_k^{[n,m]} \frac{x_<^k}{x_>^k}, \tag{2}$$

where $x_< = \min(x,x')$, $x_> = \max(x,x')$ and the coefficients $\beta_0^{[n,m]},\beta_1^{[n,m]},\ldots,\beta_{n-1}^{[n,m]}$ are implicitly given by Eq. (17) of Ref. 5. The values of the coefficients $\alpha_i^{[n,m]}$ are found numerically,[5,7] by solving the system of linear equations

$$\mathcal{V}(r_j)=\sum_{i=1}^{p} \alpha_i^{[n,m]} q^{[n,m]}(r_i,r_j). \tag{3}$$

At short range, if $r < r_1$, this gives

$$q^{[n,m]}(r,r_i)=\sum_{k=0}^{n-1} \beta_k^{[n,m]} \frac{r^k}{r_i^{m+1+k}}. \tag{4}$$

Substituted into Eq. (1), this gives the short-range extrapolation of the RP-RKHS potential as

$$V^{[n,m]}(r)=\sum_{k=0}^{n-1} d_k^{[n,m]} r^k, \tag{5}$$

where

$$d_k^{[n,m]}=\beta_k^{[n,m]} \sum_{i=1}^{p} \frac{\alpha_i^{[n,m]}}{r_i^{m+1+k}}. \tag{6}$$

The RP-RKHS procedure thus gives a potential that extrapolates to short range with a polynomial of order $n-1$. In typical applications, n is quite small (often 2). Since the true potential is usually approximately exponential at short range, the extrapolation of the RP-RKHS potential can be quite poor. The procedure should not be used in this way. In situations where the repulsive part is important (e.g., in scattering calculations) one should ensure that the *ab initio* points continue high up the repulsive wall, and not rely on the extrapolation to be accurate.

The behavior of the long-range extrapolation is more satisfactory. When $r > r_p$, Eq. (2) gives

$$q^{[n,m]}(r,r_i)=\frac{1}{r^{m+1}} \sum_{k=0}^{n-1} \beta_k^{[n,m]} \frac{r_i^k}{r^k}, \tag{7}$$

and the RP-RKHS extrapolation function has the form

$$V^{[n,m]}(r)=\sum_{k=0}^{n-1} -\frac{c_{m+1+k}^{[n,m]}}{r^{m+1+k}}, \tag{8}$$

where

$$-c_{m+1+k}^{[n,m]}=\beta_k^{[n,m]} \sum_{i=1}^{p} \alpha_i^{[n,m]} r_i^k \tag{9}$$

are the explicit expressions for the long-range coefficients. Thus if we require a potential that behaves as $C_m r^{-m}$ at long

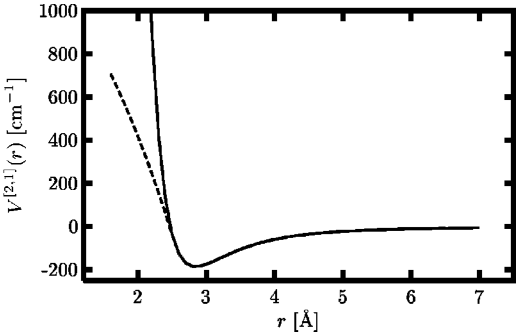

FIG. 1. Potential curves for the ground electronic state of He-Ar$^+$ generated with the RP-RKHS procedure. The full line is obtained using all the *ab initio* points; the dashed line is obtained using only points $\mathcal{V}(r)<0$, and is thus an extrapolation rather than an interpolation for $r<2.5$ Å.

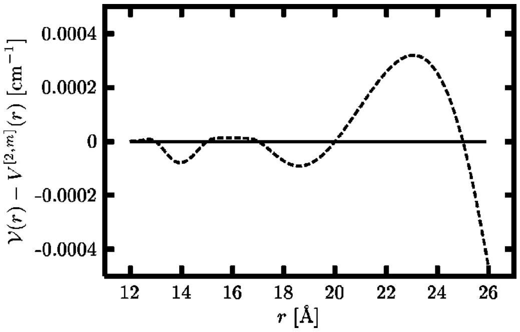

FIG. 2. Interpolation errors for He-Ar$^+$ using different RP-RKHS procedures. Solid line: interpolation with respect to r^2, using $m=1$ and $n=2$. Dashed line: interpolation with respect to r, using $m=0$ and $n=2$.

range, we must use an RP-RKHS function of the type $V^{[n,m-1]}(r)$. Although the correct behavior was noted and used by Ho and Rabitz,[5] functions such as $V^{[n,m]}(r)$ and $V^{[n,0]}(r)$ have been used as RP-RKHS interpolants in other such situations.[8–10]

In order to illustrate the points above, we consider the example of He-Ar$^+$, for which potential curves have recently been determined by Carrington *et al.*[11] The curves correlating with Ar$^+(^2P)$ can be expressed in terms of sum and difference potentials $V_0(r)$ and $V_2(r)$. To provide a set of points for interpolation, we evaluate $V_0(r)$ for the MAL1 potential of Carrington *et al.*[11] at a set of points at 0.1 Å intervals from 2 to 10 Å and at 11, 12, 13, 15, 17, 20 and 25 Å.

The He-Ar$^+$ potential has a long-range expansion of the form

$$\mathcal{V}(r)\sim-\frac{C_4}{r^4}-\frac{C_6}{r^6}+\cdots. \tag{10}$$

To prevent contamination of the long-range part by odd-order terms, we recommend interpolating with respect to $y=r^2$. Consequently, to obtain the correct leading term we must set $m=1$. From the point of view of numerical stability it is desirable to keep n as low as possible,[8] so we use $n=2$. The long-range part of the RP-RKHS potential is then of the form

$$V^{[2,1]}(r)=-\frac{c_2^{[2,1]}}{y^2}-\frac{c_3^{[2,1]}}{y^3}=-\frac{c_2^{[2,1]}}{r^4}-\frac{c_3^{[2,1]}}{r^6}, \tag{11}$$

while the short-range part is

$$V^{[2,1]}(r)=d_0^{[2,1]}+d_1^{[2,1]}y=d_0^{[2,1]}+d_1^{[2,1]}r^2. \tag{12}$$

Figure 1 shows the behavior of the RP-RKHS potentials in the repulsive region. The full line was obtained using all the points described above, extending in to $r=2.0$ Å, $\mathcal{V}(r)=3063$ cm^{-1}. The dashed line was obtained using only points for which $\mathcal{V}(r)<0$, which results in the omission of five points inside $r=2.5$ Å. The extrapolated repulsive wall is clearly a poor representation of the true potential.

At long range, the recommended interpolation procedure gives $c_2^{[2,1]}=0.6915E_ha_0^4$ and $c_3^{[2,1]}=9.97E_ha_0^6$, from Eq. (9), as the RP-RKHS counterparts of C_4 and C_6 coefficients, respectively. These values compare well with the values $0.6915E_ha_0^4$ and $8.13E_ha_0^6$ from Ref. 11. An RP-RKHS function with a different value of m would not even give r^{-4} behavior at long range.

Interpolation with respect to r^2 using $m=1$ and $n=2$, as recommended here, is much more accurate than with alternative values of m, even inside the range of the points. Figure 2 compares the error for He-Ar$^+$ from 12 to 26 Å from our recommended procedure with that from the procedure used by Ho *et al.*[8] and Schatz *et al.*[9] (i.e., interpolation with respect to r, using $m=0$ and $n=2$). It may be seen that our recommended procedure gives substantially lower errors. The maximum error is in fact a factor of 80 000 lower for the recommended procedure.

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