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Representing Potential Energy Functions by Expansions in Orthogonal Polynomials. Generalized SPF Potentials

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It long has been known that advantages attend employing, as a basic internuclear coordinate for determining a molecular potential energy surface, a variable $S = 1 - R_0/R$, where R_0 is a reference distance near to half of an equilibrium distance. For a diatomic molecule, starting from numerical or analytical representations of the energy, $W(R) = W(S)$, it is shown how to generate the analytical series, $W(S) = \sigma(S)\sum_n b_n P_n(S)$, where $P_n(S)$ are orthogonal polynomials with weight function $\sigma(S)$ over the range $(-1,1)$ for S. By rearrangement, there result the series for $W(R)$ in inverse powers of R. For neutral diatomics, the Jacobi polynomials, $P_n^{1,6}(S)$ with weight function $(1 + S)(1 - S)^6$, seem particularly appropriate when the potential for large R is of special interest.

Consider a prototypical diatomic molecule in the Born−Oppenheimer approximation, with ground-state potential energy $W(R)$ a function of the internuclear distance R and equilibrium distance R_e. Parr and White introduced[1] and Simons, Parr, and Finlan (SPF) applied and treated in some detail[2] a power series for $W(R)$ in the variable $(1 - R_e/R)$. This expansion has since seen many applications.[3−7] In the present paper, we refine, systematize, and extend the SPF approach.

We adopt as the expansion variable a generalization of the SPF variable

$$S \equiv 1 - R_0/R \tag{1}$$

with R_0 as a reference point more or less near R_e. Then $S = \{-\infty, -1, 0, 1\}$ for $R = \{0, R_0/2, R_0, \infty\}$. Note that the transformation of variables from R to S forces the simple pole at $R = 0$ to the edge of the real line without increasing its order, whereas at the same time the problem of discerning the asymptotic decay of $W(R)$ as $R \to \infty$ has been changed to the problem of finding the behavior of $W(S)$ at $S = 1$. We now set out to suitably represent $W(S)$ as a power series

$$W(S) \equiv \sum_n a_n S^n \tag{2}$$

or some truncation thereof. We hope to thereby find a useful analytical expression for $W(S)$ that can be systematically improved as the amount of data available increases. We also want to obtain a reasonable potential energy surface even when the number of terms included is small. In Figure 1 are shown $W(R)$ and $W(S)$ for the hydrogen molecule.

The original SPF work well demonstrates the power and the promise of eq 2. See, for example, Figure 5 in SPF,[2] which compares a sixth-order potential of the form of eq 2 with the RKR potential for carbon monoxide. Input for the SPF calculations were four Dunham coefficients and two boundary conditions at $S = 1$ ($R \to \infty$). The dissociation energy for carbon monoxide was predicted within seven percent of the experimental value.

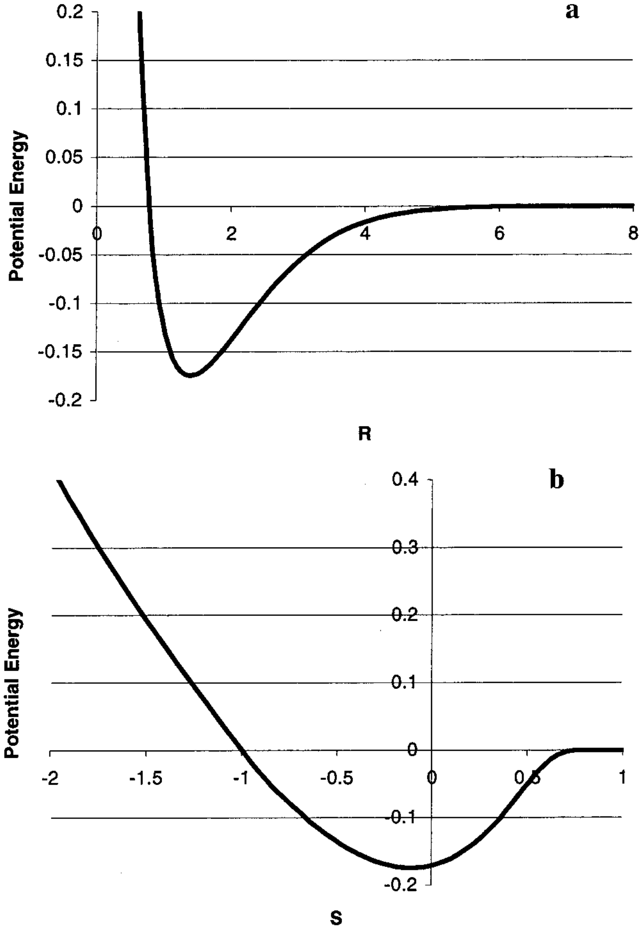

Figure 1. Potential energy surface for the hydrogen molecule.[23] (a) $W(R)$ vs R. (b) $W(S)$ vs S.

The method can be improved, and made completely systematic, with the modifications we now describe. We may assume $W(S)$ is known in advance, whether from ab initio calculations, inference from experiment, or otherwise. We choose to use information about $W(S)$ only in the "significant" region from $R = R_0/2$ to $R \to \infty$, that is, the region from $S = -1$ to 1. This suggests eschewing series in S in favor of series of orthogonal

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polynomials in S, $P_n(S)$, orthogonal over the interval $(-1,1)$ with respect to some appropriate weighting factor, $\sigma(S)$. Thus, we have

$$W(S) = \sigma(S)\sum_n b_n P_n(S) \tag{3}$$

and

$$b_n \equiv \int_{-1}^{1} P_n(S)W(S)\,\mathrm{d}S \tag{4}$$

For a given $W(S)$, R_0, and choice of orthogonal polynomials, the coefficients b_n are uniquely determined by this procedure, and the procedure is systematic and readily implemented.

A reasonable (though not mandatory) choice for $R_0/2$ is the turning point on the potential energy surface, $W(R_0/2) = W(\infty) = 0$, with the last equality setting our choice of energy zero. One must choose among the available sets of polynomials orthogonal over $(-1,1)$; in the limit, different choices should give the same $W(S)$.

By inserting eq 1 into eq 3, one finds $W(R)$ as a sum of polynomials in $(1 - R_0/R)$, from which rearrangement yields a sum of inverse powers of R. (More simply, noting that $S - 1 = - R_0/R$, the coefficients in the $1/R$ expansion may be obtained from the coefficients of the Taylor series expansion of $W(S)$ about $S = 1$.) The coefficients of the Taylor series, in turn, may be efficiently computed using the recurrence relation for $\mathrm{d}P_n(S)/\mathrm{d}S$.) In principle, even the very small (but important) long-range terms in $W(R)$ (such as $1/R^6$) will be determined correctly by this procedure.

Appealing as weight functions are the Jacobi polynomials, $P_n^{\alpha,\beta}(S)$, $n = 0, 1, 2, ...$,[8] for which the weight function is

$$\sigma(S) = (1 + S)^{\alpha}(1 - S)^{\beta} \tag{5}$$

so that

$$W(S) = [(1 + S)^{\alpha}(1 - S)^{\beta}]\sum_n b_n P_n^{\alpha,\beta}(S) \tag{6}$$

with

$$b_n \equiv \int_{-1}^{1} P_n^{\alpha,\beta}(S)W(S)\,\mathrm{d}S \tag{7}$$

The b_n are most readily computed if the input potential energy surface is evaluated at the abscissas of the appropriate Gauss–Jacobi quadrature formula.[9,10]

Experience will tell which choices of α and β will be best for a particular application. Consider first $\alpha = \beta = 0$, $\sigma(S) = 1$. Then

$$W(S) = \sum_{n=0}^{\infty} b_n P_n(S) \tag{8}$$

and

$$b_n \equiv \int_{-1}^{1} P_n(S)W(S)\,\mathrm{d}S \tag{9}$$

where the $P_n(S)$ are the classic Legendre polynomials. The full expansion of eq 8 is essentially (but see the next paragraph) the SPF expansion already known to be useful and quite accurate.[2] Truncated at three terms, it is the reasonably good Fues potential,[11] which is a quadratic in $1/R$. Note that eq 9 provides immediate access to the parameters in the potential, though when the expansion is severely truncated one would generally prefer empirical values of the coefficients.

Consider next $\alpha = \beta = 1$, $\sigma(S) = (1 + S)(1 - S)$, producing

$$W(S) = (1 + S)(1 - S)\sum_n b_n P_n^{\alpha,\beta}(S) \tag{10}$$

Because $(1 + S)(1 - S) = (R_0/R) - 2)(R_0/R)$, the zeroth order term here already recovers the form of the Fues potential. This formula provides an efficient way to generate the SPF potential.

As a more drastic change from the original SPF method, accounting for the true $R \to \infty$ behavior and responding to our desire to extract long-range coefficients from accurate potentials, we take β to be the leading-order term in the asymptotic series in $1/R$ (mimicking the way $W(R) \to 0$ as $R \to \infty$); for a neutral diatomic, $\beta = 6$. If one chooses R_0 so that $W(R_0/2) = 0$, it is also appropriate to take $\alpha = 1$ (which mimics the way $W(R) \to 0$ as $R \to (R_0/2)$. (If $W(R_0/2) \neq 0$, then $\alpha = 0$ is more appropriate.) Then, for a neutral diatomic molecule, we will have $\sigma(S) = (1 + S)(1 - S)^6$

$$W(S) = [(1 + S)(1 - S)^6]\sum_n b_n P_n^{1,6}(S) \tag{11}$$

and

$$b_n \equiv \int_{-1}^{1} P_n^{1,6}(S)W(S)\,\mathrm{d}S \tag{12}$$

Implementation of eqs 8, 10, and 11 are equally easy. Note that because $(1 + S)(1 - S)^6 = (R_0/R - 2)(R_0/R)^6$ the series generated using eq 11 yield, upon rearrangement, asymptotic series in $(R_0/R)^6$ and higher powers of (R_0/R). Such expansions overcome the primary shortcoming associated with the original SPF method: the difficulty of satisfying the appropriate asymptotic constraints.[12]

Finally, one could go on to a weight function which recovers both the $R \to 0$ and the $R \to \infty$ limits, for example

$$\sigma(S) = \frac{(1 + S)(1 - S)^6}{((S + a)^2 + b^2)^3} \tag{13}$$

where a and b are chosen to produce the correct asymptotic decay, $W(R) \sim Z_1Z_2/R$ as $R \to 0$ and $W(S) \sim (Z_1Z_2/R_0)\,(1 - S)$ as $S \to -\infty$. The set of orthogonal polynomials associated with eq 13 is found through repeated application of the generalized Christoffel theorem,[13] which tells how recursion coefficients are modified when $\sigma(S)$ is modified by a polynomial divisor.

The preceding methods for forcing asymptotic constraints on potential energy functions are similar to the “reproducing kernel” techniques employed by Ho, Rabitz, and co-workers.[14,15] Indeed, the orthogonal polynomial expansion may be generated using the reproducing kernel from the theory of orthogonal polynomials[16]

$$W(S) = \sigma(S)\int_{-1}^{1} K_M(S,S')W(S')\,\mathrm{d}S' \tag{14}$$

where

$$K_M(S,S') \equiv \sum_{n=0}^{M} P_n(S)P_n(S') \equiv \frac{1}{a_M}\cdot\frac{P_M(S')P_{M+1}(S) - P_M(S)P_{M+1}(S')}{S - S'} \tag{15}$$

Here, $P_n(S)$ are the orthogonal polynomials associated with the measure $\sigma(S)$ and a_M is the recursion coefficient for the orthonormal polynomials associated with the weight $\sigma(S)$

$$P_{M+1}(S) = (a_M S + b_M)P_M(S) - c_M P_{M-1}(S) \qquad (16)$$

For any $\sigma(S)$ of interest, recursion coefficients (thence orthogonal polynomials) can be generated using standard subroutines;[17] this provides computationally efficient techniques for generating representations of the potential energy surface.

Rearrangements to series in $1/R$ are routine for any of the truncated forms. In the limit where the expansions are not truncated, there result asymptotic series in $1/R$: the very $1/R$ series that have been the subject of so much attention in the past.[18]

Rapid convergence of any of these formulas to the original given $W(S)$ is guaranteed by the fact that, as illustrated in Figure 1, $W(S)$ is smooth on $[-1,1]$. In particular, because $W(S)$ is differentiable to all orders, the asymptotic decay of the expansion coefficients, b_n, is faster than any polynomial in n^{-1}. (In more detail, $\lim_{n\to\infty}(b_n/n^\kappa) \to 0$ for any finite κ.)[19] Accurate approximation of the potential energy surface should result even when the expansions are truncated at low order.

The fact that information from $S < -1$ has been not been used as input does not preclude the final calculated $W(S)$ from being accurate in the repulsive portions of the surface: This is because analytic functions which are identical on any interval of finite length are identical over their entire extent of analyticity; if $W(S)$ is analytic in some ellipse containing the interval $[-1,1]$, then $W(S)$ will be accurately approximated within this ellipse. (One may argue that truncated series should quickly approach this optimal result: The asymptotic decay of the expansion coefficients for functions analytic in an ellipse decay as geometric series, $|b_n| \sim p^n$ where $0 \le p < 1$ depends on the size of the ellipse.[19]) In the not unreasonable (but, to the authors' knowledge, unproved) case in which $W(S)$ is everywhere analytic (excepting, of course, $S \to \pm\infty$), the orthogonal expansion technique proposed here gives an accurate depiction of the entire potential energy surface and the magnitudes of the expansion coefficients decay faster than any geometric series.

These results certainly improve the methods for dealing with SPF potentials for diatomic molecules. It will be highly interesting to apply the same ideas to polyatomic molecules. In the spirit of the "central force field" of the classical theory of vibrations,[20] take the set of all scalar internuclear distances as internal coordinates and replace each internuclear distance with an appropriate SPF coordinate. Note that $^1/_2N(N-1) \ge 3N-6$ for $N \ge 3$, with equality holding for $N = 3$ and 4. Provided the redundancy problem is addressed, central force coordinates can also be used for $N > 4$.[21,22]

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References and Notes

(1) Parr, R. G.; White, R. J. *J. Chem. Phys.* **1968**, *49*, 1059.
(2) Simons, G.; Parr, R. G.; Finlan, J. M. *J. Chem. Phys.* **1973**, *59*, 3229.
(3) Ritschel, T.; Mahapatra, S.; Zulicke, L. *Chem. Phys.* **2001**, *271* (1−2), 155−164.
(4) Molski, M. *Acta Phys. Polonica A* **1999**, *96* (6), 713−723.
(5) Herman, M.; Lievin, J.; Vander Auwera, J.; Campargue, A. *Adv. Chem. Phys.* **1999**, *108*, 1.
(6) Koput, J.; Carter, S.; Handy, N. C. *Chem. Phys. Lett.* **1999**, *301* (1−2), 1−9.
(7) Chambaud, G. *J. Chim. Phys. Physico-Chim. Biol.* **1998**, *95* (8), 1892−1924.
(8) Temme, N. M. *Special Functions: An Introduction to the Classical Functions of Mathematical Physics*; Wiley: New York, 1996.
(9) Gautschi, W. *ACM Trans. Math. Software* **1998**, *24* (3), 355−357.
(10) Gautschi, W. *ACM Trans. Math. Software* **1994**, *20* (1), 21−62.
(11) Borkman, R. F.; Parr, R. G. *J. Chem. Phys.* **1968**, *48*, 116−1126.
(12) Schatz, G. C. *Rev. Mod. Phys.* **1989**, *61* (3), 669−688.
(13) Gautschi, W. In *Numerical Integration*; Hammerlin, G., Ed.; ISNM 57; Birkhauser: Basel, 1982; pp 89−106.
(14) Hollebeek, T.; Ho, T. S.; Rabitz, H. *J. Chem. Phys.* **1997**, *106* (17), 7223−7227.
(15) Ho, T. S.; Rabitz, H. *J. Chem. Phys.* **1996**, *104* (7), 2584−2597.
(16) Temme, N. M. *Special Functions: An Introduction to the Classical Functions of Mathematical Physics*; Wiley: New York, 1996.
(17) Gautschi, W. *ACM Trans. Math. Software* **1994**, *20* (1), 21−62.
(18) *Diatomic Interaction Potential Theory*; Goodisman, J.; Academic Press: New York, 1973; Vol. 1.
(19) Timan, A. F. *Theory of Approximation of Functions of a Real Variable*; Dover: New York, 1994; p 571.
(20) Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectroscopy*; Dover: New York, 1994; p 173.
(21) Thompson, K. C.; Jordan, M. J. T.; Collins, M. A. *J. Chem. Phys.* **1998**, *108* (20), 8302−8316.
(22) Sun, C. E.; Parr, R. G.; Crawford, B. L., Jr. *J. Chem. Phys.* **1949**, *17* (9), 840.
(23) Kolos, W.; Szalewicz, K.; Monkhorst, H. J. *J. Chem. Phys.* **1986**, *84* (6), 3278−3283.