

COMMENT

COMMENT ON "PERTURBATIONAL AND VARIATIONAL TREATMENTS OF THE MORSE OSCILLATOR"

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In a recent article, Cooper [1] has presented an elegant treatment of the Morse oscillator in terms of a perturbation from a harmonic oscillator potential. What was novel about his approach was the use of the Morse variable  $Q = (1 - e^{-\alpha r})/\alpha$  as the coordinate for the zero-order harmonic oscillator Hamiltonian. In terms of this coordinate and its conjugate momentum, the Morse oscillator Hamiltonian contains terms only up to quartic power of momentum and the coordinate, which means that the Hamiltonian matrix in a harmonic basis is banded with states differing by more than four quanta having zero matrix elements. This is of obvious utility for perturbation calculations where the sum over intermediate

states is finite. In contrast, when the bond displacement coordinate is used, the Hamiltonian in a harmonic basis has matrix elements that are exponentially damped but finite for all values of the quantum number difference.

For variational calculations, what matters most importantly is the computational effort to compute matrix elements and the rate of convergence. Cooper presented results for the rate of convergence of a "typical" Morse oscillator problem using a finite basis of harmonic functions in the Morse variable. In this comment, I would like to compare that convergence on the same problem, but using harmonic functions in the bond displacement coordinate.

Table 1  
 Comparison of the error in the energy of a Morse oscillator with  $x=0.0229$  calculated variationally using a finite basis set of harmonic oscillator functions in the Morse variable and in the bond displacement variable.  $N$  is the maximum harmonic basis function used, and errors are given in units of the harmonic frequency which is the same for the two methods

$\nu$	Morse variable <sup>a)</sup>					
	$N=25$	$N=50$	$N=100$	$N=200$	$N=400$	$N=500$
5	$1.5 \times 10^{-3}$	$10^{-6}$	$10^{-10}$	$10^{-13}$	$10^{-13}$	$10^{-13}$
10	0.7394	0.0379	$2 \times 10^{-4}$	$10^{-7}$	$10^{-10}$	$10^{-11}$
15	4.863	1.373	0.2713	0.0257	0.0010	0.0003
20	14.16	5.363	2.402	1.061	0.4644	0.3540
Bond displacement coordinate						
	$N=25$	$N=50$	$N=100$	$N=200$	$N=400$	$N=500$
5	$1.3 \times 10^{-4}$	$1.0 \times 10^{-10}$	$< 10^{-13}$	$< 10^{-13}$	$< 10^{-13}$	$< 10^{-13}$
10	0.70	0.012	$1.8 \times 10^{-8}$	$< 10^{-13}$	$< 10^{-13}$	$< 10^{-13}$
15	4.59	1.33	0.096	$6.1 \times 10^{-6}$	$< 10^{-13}$	$< 10^{-13}$
20	11.67	5.21	1.81	0.38	0.024	$5.9 \times 10^{-3}$

<sup>a)</sup> Data taken from table 1 of ref. [1].

Consider a Morse potential with harmonic frequency  $\omega$  (in  $\text{cm}^{-1}$ ) and anharmonicity  $x$  such that the "exact" eigenvalues are given by [2]

$$V(r) = D_e(1 - e^{-\alpha r})^2,$$

$$E(v) = \omega(v + \frac{1}{2}) - \omega x(v + \frac{1}{2})^2.$$

Matrix elements of the Morse potential can be evaluated by using the fact that the matrix elements of the Morse variable may be evaluated by using

$$\langle n+k | e^{-\alpha r} | n \rangle$$

$$= e^{x/2} x^{k/2} \sum_{j=0}^n \frac{\sqrt{n!(n+k)!} x^j}{j!(k+j)!(n-j)!},$$

$$\langle n+k | e^{-2\alpha r} | n \rangle$$

$$= e^{2x} (4x)^{k/2} \sum_{j=0}^n \frac{\sqrt{n!(n+k)!} (4x)^j}{j!(k+j)!(n-j)!},$$

where  $x$  is the anharmonicity. The rate of convergence depends upon the parameter  $x$  alone, with a value of 0.0229 used by Cooper as typical for an XH diatomic, which results in 22 bound states. We diagonalized the Morse oscillator in a harmonic basis of up to 501 functions and in table 1 compare the energy errors with those given by Cooper in table 1 of his paper. Following Cooper, we give energy differences in scaled units by dividing by the harmonic frequency. The rate of convergence is clearly faster when

the bond coordinate is used.

While the greater number of nonzero matrix elements when the bond displacement coordinate is used results in a greater amount of time being required to set up a matrix of given size, the diagonalization dominates the time required. Thus, the number of functions required for a given level of convergence is the figure of merit. Our comparison, however, does not include consideration of continued fraction or other such methods that make use of the banded character of the Morse variable Hamiltonian matrix which may lead to the secular determinate being solved much more efficiently than in the bond displacement coordinate treatment.

One surprising observation in light of the above results is that the rms energy uncertainty of the initial basis states is higher for the harmonic functions in the displacement coordinate than in the Morse coordinate. In particular, if we look at  $v=10$ , the energy uncertainty is 5.31 in scaled units for the Morse coordinate, while 7.51 for the displacement coordinate.

## References

- [1] I.L. Cooper, Chem. Phys. 112 (1987) 67.
- [2] D. ter Haar, Phys. Rev. 70 (1946) 222.