Inverse Perturbation Analysis: Improving the Accuracy of Potential Energy Curves [1]

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The equation for the first-order energy correction is used inversely to find the perturbation responsible for the energy correction. In the specific application to the calculation of a potential energy curve from the spectroscopic term values, the sought perturbation is a correction to an approximate potential curve. Consequently, an approximate potential curve (e.g. an RKR (Rydberg–Klein–Rees) curve) can be improved until the eigenvalues calculated for this curve agree with the spectroscopic term values within the experimental uncertainty. Results are given for the $X^2\Sigma^+$ state of HgH.

I. INVERSE PERTURBATION ANALYSIS

According to perturbation theory, the first-order energy correction to some nth state, E_n', is calculated

$$E_n' = \langle \psi_n^0 | \mathbf{H}' | \psi_n^0 \rangle. \tag{1}$$

Equation (1) is utilized when the total Hamiltonian, $\mathbf{H}$, in the Schroedinger equation,

$$\mathbf{H}\psi_n = E_n\psi_n, \tag{2}$$

is composed of a major zeroth-order contribution, $\mathbf{H}^0$, and a small perturbation, $\mathbf{H}'$,

$$\mathbf{H} = \mathbf{H}^0 + \mathbf{H}'. \tag{3}$$

The wavefunctions in Eq. (1), assumed to be normalized, are the eigenfunctions of the zeroth-order Hamiltonian:

$$\mathbf{H}^0\psi_n^0 = E_n^0\psi_n^0. \tag{4}$$

In the usual application of Eq. (1), a first-order energy correction is sought for a known perturbation to a known zeroth-order Hamiltonian. Such a calculation is successful if the perturbation is small. The authors suggest using Eq. (1) in an inverse manner, namely to find an unknown perturbation from a known energy correction. Again success is expected if the perturbation is small.

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II. APPLICATION TO POTENTIAL ENERGY CURVE ANALYSIS

In the remainder of this paper we will examine the application of inverse perturbation analysis (IPA) to the problem of calculating an accurate potential energy curve from its spectroscopic term values. The pertinent equation is the radial Schroedinger equation:

$$\left(-\frac{\hbar}{4\pi\mu c}\frac{d^2}{dr^2} + U_J(r)\right)R_{v,J}(r) = E_{v,J}R_{v,J}(r). \tag{5}$$

In Eq. (5) r is the internuclear distance in cm, μ is the reduced mass of the nuclei in grams, $U_J(r)$ is the effective potential governing the vibration of the nuclei in cm^{-1}, all other constants have their usual meanings in cgs units,[3] and v and J are the vibra-

[3] Unless specifically noted otherwise, cgs units are used throughout the paper except for energies which are expressed in cm^{-1}.

tional and rotational quantum numbers, respectively. $U_J(r)$ is composed of two terms, a rotationless potential energy term, $U_0(r)$, and a centrifugal potential term whose form depends on the particular angular momentum coupling case which is applicable for the system under consideration. For example, for a $^1\Sigma$ state we have

$$U_J(r) = U_0(r) + \frac{\hbar}{4\pi\mu c}\frac{J(J+1)}{r^2}. \tag{6}$$

One would like to find the exact rotationless potential producing the observed spectroscopic term values.

If one has a good approximate (zeroth order) rotationless potential energy function, $U_0^0(r)$, then the actual rotationless potential energy function and the approximate rotationless potential energy function differ by a correction, $\Delta U_0(r)$,

$$U_0(r) = U_0^0(r) + \Delta U_0(r). \tag{7}$$

The true Hamiltonian and the approximate (zeroth order) Hamiltonian differ by the same correction,

$$\mathbf{H} = \mathbf{H}^0 + \Delta U_0(r), \tag{8}$$

since the kinetic energy operator is identical in both. Consequently, the correction needed to improve an approximate potential can be treated as a perturbation to the Hamiltonian formed with the approximate potential. Hence, using Eq. (1),

$$E_{v,J}' = \langle R_{v,J}^0 | \Delta U_0 | R_{v,J}^0 \rangle \quad \begin{matrix} v = 0, 1, 2, \ldots, \\ J = 0, 1, 2, \ldots, \end{matrix} \tag{9}$$

where the radial wavefunctions in Eqs. (9) are the normalized solutions of the zeroth-order radial Schroedinger equation,

$$\left(-\frac{\hbar}{4\pi\mu c}\frac{d^2}{dr^2} + U_J^0(r)\right)R_{v,J}^0(r) = E_{v,J}^0 R_{v,J}^0(r) \quad \begin{matrix} v = 0, 1, 2, \ldots, \\ J = 0, 1, 2, \ldots. \end{matrix} \tag{10}$$

Collectively, Eqs. (9) form a set of linear integral equations to be solved for the unknown kernel, $\Delta U_0(r)$. A set of ordinary linear equations can be obtained by expanding the

kernel in some suitable basis,

$$\Delta U_0(r) = \sum_i c_i f_i(r). \tag{11}$$

The resulting set of linear equations,

$$E_{v,J}' = \sum_i c_i \langle R_{v,J}^0 | f_i | R_{v,J}^0 \rangle \quad \begin{aligned} v &= 0, 1, 2, \ldots, \\ J &= 0, 1, 2, \ldots, \end{aligned} \tag{12}$$

are to be solved for the expansion coefficients, the c_i's.

Actually, the first-order energy corrections in Eqs. (12) are not known. However, they can be approximated as being the entire energy correction, namely the difference between the observed spectroscopic term values and the appropriate eigenvalues calculated for the approximate potential using Eqs. (10)

$$E_{v,J}' \approx E_{v,J} - E_{v,J}^0. \tag{13}$$

Substitution of the approximation into Eqs. (12) yields the actual set of equations to be solved in this application of IPA,

$$E_{v,J} - E_{v,J}^0 = \sum_i c_i \langle R_{v,J}^0 | f_i | R_{v,J}^0 \rangle \quad \begin{aligned} v &= 0, 1, 2, \ldots, \\ J &= 0, 1, 2, \ldots. \end{aligned} \tag{14}$$

In the practical application of Eqs. (14), three approximations are made. The first was already mentioned in regards to Eq. (13). The second approximation is that the expansion of ΔU_0 in Eq. (11) has to be truncated to a finite expansion. The third approximation is that the radial Schroedinger equations, Eqs. (10), have to be solved numerically. Because of these approximations it is not expected that the system of linear equations, Eqs. (14), can be satisfied exactly. Instead these equations are solved in a least-squares manner for a "best" set of expansion coefficients. Consequently, the potential energy correction, $\Delta U_0(r)$, calculated with these "best" expansion coefficients will not be the true correction but only a partial correction. This correction can be used to calculate a new, improved approximate potential, $U_0^0(r)$, and the whole procedure can be iterated with this improved approximate potential.

In summary, the procedure flows according to the following steps.

(1) Obtain some initial approximate potential, $U_0^0(r)$ (e.g. an RKR potential).
(2) Solve Eqs. (10) for the zeroth-order eigenvalues and eigenfunctions.
(3) Calculate the $E_{v,J}'$'s using Eq. (13).
(4) If the $|E_{v,J}'|$'s are all less than some desired threshold (e.g. the experimental uncertainty), stop; if not, continue.
(5) Calculate the expectation values, $\langle R_{v,J}^0 | f_i | R_{v,J}^0 \rangle$.
(6) Solve the system of linear equations, Eqs. (14), for the "best" set of expansion coefficients.
(7) Update the approximate potential
$$U_0^0(\text{new}) = U_0^0(\text{old}) + \Delta U_0.$$
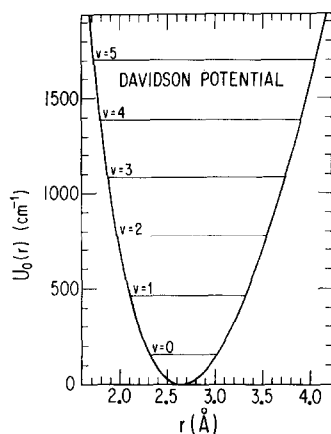(8) Go to Step 2.

FIG. 1. The Davidson potential.

III. TESTING THE INVERSE PERTURBATION ANALYSIS

A simple test of the above theory is possible. One can start with a given potential, purposely distort this potential to obtain an initial approximate potential, and then apply the inverse perturbation analysis to the approximate potential to see if it yields the original potential.

Such a test was conducted. For this test, the original known potential was chosen to be the Davidson potential (1),

$$U_0(r) = ar^2 + b/r^2 - 2(ab)^{\frac{1}{2}}, \tag{15}$$

although any reasonable potential could have been selected as a starting point. The

TABLE I

ACCURACY OF THE APPROXIMATE POTENTIAL ENERGY CURVE

r (in Å)	$U_0(r) - U_0^o(r)$ (in cm^{-1})	
	INITIALLY	AFTER 1st ITERATION
0.5	60	-2
1.0	13	-0.1
1.5	-5	0.04
2.0	-2	0.03
2.5	-0.3	-0.006
3.0	0.5	-0.008
3.5	1	-0.02
4.0	1	-0.02
4.5	1	-0.01
5.0	1	-0.006

TABLE II

ACCURACY OF THE EIGENVALUES FOR THE APPROXIMATE POTENTIAL

J	$\left\| E_{v,J} - E_{v,J}^{o} \right\|^{a}$ (in cm^{-1})	
	INITIALLY	AFTER 1st INTERATION
0	< 0.002	< 0.002
1	0.002	"
2	0.011	"
3	0.018	"
4	0.029	"
5	0.042	"
6	0.057	"
7	0.075	"
8	0.092	"

^{a}Numerical accuracy used for solving radial Schroedinger Equation = ±0.002 cm^{-1}.

eigenvalues of this Davidson potential, which can be found analytically,

$$E_{v,J} = 4\left(\frac{\hbar a}{4\pi\mu c}\right)^{\frac{1}{2}}\left[(v + \tfrac{1}{2}) + \frac{1}{2}\left(\frac{4\pi\mu cb}{\hbar} + J(J + 1) + \tfrac{1}{4}\right)^{\frac{1}{2}}\right] - 2(ab)^{\frac{1}{2}}, \qquad (16)$$

were consequently treated as being the observed spectroscopic term values. The initial approximate potential to this Davidson potential was found by subtracting an adjustment function, δU_0,

$$U_0^0(r) = U_0(r) - \delta U_0(r). \qquad (17)$$

The adjustment function was selected to produce an approximate potential horizontally shifted from the original potential in the neighborhood of the minimum, a shift calculated to be representative of what one might expect of a first-order Dunham analysis according to Kosman and Hinze (2). The inverse perturbation analysis was then applied to $U_0^0(r)$.

Specifically, Fig. 1 shows the Davidson potential which was used for the test with $a = 313.5$ [cm^{-1}/Å^2] and $b = 15365$ [cm^{-1} Å^2] chosen to approximately fit the $A^1\Sigma^+$ curve of LiH. The reduced mass chosen was also appropriate for LiH. The actual form of the adjustment function used was

$$\delta U_0(r) = -15.3697/r^2 + 2.1942 + 9.79\cdot10^{-5}r^2, \qquad (18)$$

where r is in Å. The form of the potential correction function, $\Delta U_0(r)$, was chosen to be similar to that of $\delta U_0(r)$,

$$\Delta U_0(r) = c_{-2}/r^2 + c_{-1}/r + c_0 + c_1r + c_2r^2. \qquad (19)$$

Consequently, $\Delta U_0(r)$ could have been calculated exactly to equal $\delta U_0(r)$. Although this was not the case, the results obtained nevertheless indicate the validity and accuracy of the inverse perturbation analysis.

A. *Error in the Approximate Potential Before and After Improvement*

Table I shows the deviation of the approximate potential from the Davidson potential before and after the first iteration. Note the substantial improvement in the accuracy of the approximate potential curve.

B. *The Error in the Eigenvalues Before and After Improvement*

The eigenvalues calculated for the initial approximate potential are in excellent agreement with those for the original Davidson potential for the $J = 0$ rotational state. This is expected since the two curves differed primarily by a horizontal translation. But all the vibrational levels calculated for higher J values deviate from those of the original Davidson potential by a constant amount. This constant deviation increases as J increases. However, after the first iteration of the IPA all of the calculated vibrational–rotational energy levels agree with those of the original Davidson potential within the numerical accuracy used for solving the radial Schroedinger equation. These results are shown in Table II.

The reported improvement was obtained by using the eigenfunctions and eigenvalues for $v = 0$ through 13 each with $J = 0$ through *8*, which clearly yields a highly over-determined system of linear equations of type Eq. (14). Fewer values would have been sufficient for the analytical test case, and we could have chosen a larger perturbation, with which more than one iteration would have been required. However, we did not deem it necessary to carry on more extensive tests on the model potential chosen; rather we wanted to test the method on a real system.

IV. APPLICATION OF THE INVERSE PERTURBATION ANALYSIS TO THE $X^2\Sigma^+$ STATE OF HgH

As noted in the authors' previous paper (*2*), the inaccuracy in a semiclassically determined potential energy curve is reduced mass dependent; the error is only expected to be significant for diatomic molecules with small reduced masses. Then for these molecules in particular, the inverse perturbation analysis may yield significant improvement when applied to their semiclassically determined approximate potentials.

HgH is one such molecule. Its $X^2\Sigma^+$ state possesses only five observed vibrational levels; consequently, the G_v and B_v expansions, needed for a semiclassical analysis, are rather short. Furthermore, the ground state of HgH is quite anharmonic. For these reasons, the $X^2\Sigma^+$ state of HgH appears ideally suited for the application of the inverse perturbation analysis.

Excellent experimental data are available for the vibrational–rotational term values of the $X^2\Sigma^+$ state (*3–8*). The spectroscopically observed term values used in the present analysis are those given by Porter (*6*) and Eakins and Davis (*8*).

The spin coupling in the $X^2\Sigma^+$ state of HgH behaves according to Hund's case b (*9*). The total angular momentum quantum number, J, assumes two possible values for

each nonzero rotational quantum number excluding spin, N, namely $J = N + \frac{1}{2}$ and $J = N - \frac{1}{2}$. The doublet splitting for each N can be reduced to a single rotational level by subtracting the spin contribution from the component with $J = N + \frac{1}{2}$; thus,

$$E_{v,N} = F_1(v, N) - \tfrac{1}{2}\gamma N, \tag{20}$$

where

$$\gamma = [F_1(v, N) - F_2(v, N)]/(N + \tfrac{1}{2}). \tag{21}$$

In Eqs. (20) and (21), F_1 is the component with $J = N + \frac{1}{2}$ and F_2 is the component with $J = N - \frac{1}{2}$. The spin reduced vibrational–rotational term values, the $E_{v,N}$'s, are considered to be the eigenvalues of the radial Schroedinger equation with the effective potential

$$U_N(r) = U_0(r) + (\hbar/4\pi\mu c)[N(N + 1)/r^2]. \tag{22}$$

The initial approximate potential curve was determined by a Rydberg–Klein–Rees (RKR) analysis (10–12) with the term values fitted by the polynomial expansions

$$G_v = -671.288 + 1384.092(v + \tfrac{1}{2}) - 80.9044(v + \tfrac{1}{2})^2$$
$$- 3.4883(v + \tfrac{1}{2})^3 - 1.5413(v + \tfrac{1}{2})^4, \tag{23}$$

and

$$B_v = 5.67853 - 0.68905(v + \tfrac{1}{2}) + 0.26427(v + \tfrac{1}{2})^2$$
$$- 0.092617(v + \tfrac{1}{2})^3 + 0.0047833(v + \tfrac{1}{2})^4. \tag{24}$$

These expansions were then used in the RKR analysis to determine the classical turning points, r_{min} and r_{max},

$$r_{min} = (f^2 + f/g)^{\frac{1}{2}} - f, \tag{25}$$

$$r_{max} = (f^2 + f/g)^{\frac{1}{2}} + f, \tag{26}$$

where

$$f = \tfrac{1}{2}(r_{max} - r_{min}) = (\hbar/4\pi\mu c)^{\frac{1}{2}} \int_{v_{min}}^{v} [G(v) - G(v')]^{-\frac{1}{2}} dv', \tag{27}$$

$$g = \tfrac{1}{2}(r_{max}^{-1} - r_{min}^{-1}) = (4\pi\mu c/\hbar)^{\frac{1}{2}} \int_{v_{min}}^{v} B(v')[G(v) - G(v')]^{-\frac{1}{2}} dv'. \tag{28}$$

But the analysis was not trusted beyond the $v = 3$ level, because the short expansion used in Eq. (23) cannot adequately represent G_v. In fact, the G_v in Eq. (23) has a maximum between $v = 3$ and $v = 4$. Thus the potential curve was extrapolated beyond the $v = 3$ level. A possibly better starting RKR curve could have been obtained by using mass reduced quantum numbers and all the isotopic data available for HgH, HgD, and HgT, but for our test this was not deemed necessary.

The inverse perturbation analysis proved to be very dependent on the expansion of $\Delta U_0(r)$. The expansion given by Eq. (19) was inadequate. After three iterations the eigenvalues for the $v = 0$ level were all vastly improved, but the higher vibrational levels were not converging. Adding r^3 and r^4 terms to the expansion did not help much. Convergence was gained by switching to Legendre polynomials transformed to be orthogonal

TABLE III

$X^2\Sigma^+$ State of HgH

| N | $E_{v,N} - E^o_{v,N}$ (in cm^{-1})[a] | | | | | | | | | |
| | v = 0 | | v = 1 | | v = 2 | | v = 3 | | v = 4 | |
	RKR	IPA[b]	RKR	IPA	RKR	IPA	RKR	IPA	RKR[c]	IPA
0	-1.89	0.09	11.51	-0.01	3.40	0.02	-1.02	-2.35		2.03
2	-2.10	0.02	11.59	0.00	3.45	-0.02	-1.42	-2.55		1.20
4	-2.45	0.01	11.73	-0.01	3.65	-0.02	-2.60	-2.88		-1.06
6	-2.97	0.00	11.93	-0.03	3.91	-0.04	-5.56	-2.91		-5.64
8	-3.65	0.00	12.19	-0.03	4.28	0.00	-14.39	-1.58		
10	-4.49	0.00	12.42	-0.02	4.70	0.06				
12	-5.47	-0.02	12.57	-0.01	5.10	0.19				
14	-6.55	-0.04	12.57	0.00	4.77	0.25				
16	-7.67	0.00	12.27	-0.01	0.57	-1.41				
18	-8.76	-0.05	11.60	0.01						
20	-9.73	-0.03	10.10	0.06						
22	-10.48	0.02	6.45	0.16						
24	-10.96	0.06								
26	-11.17	0.10								

[a] Values of $E_{v,N}$ from Porter (6) and Eakin and Davis (8).

[b] Inverse Perturbation Analysis.

[c] No v = 4 levels were found for the initial RKR curve

on the interval $[a, b]$

$$\Delta U_0(r) = \sum_{i=0}^{12} c_i P_i(x), \qquad (29)$$

where

$$x = [2r - (a + b)]/(b - a). \qquad (30)$$

The interval $[a, b]$ is selected to correspond to the range over which the radial wave-functions are expected to be large. For the $X^2\Sigma^+$ state of HgH the interval was chosen to be $[1.0 \text{ Å}, 5.5 \text{ Å}]$. We would expect faster convergence had we chosen a set of orthogonal functions which exhibit the proper behavior in the limit as r approaches zero and infinity, however we did not test this.

The results are shown in Table III. This table shows the deviation between the observed spectroscopic term values and the calculated eigenvalues for both the initial RKR potential and the potential improved by the inverse perturbation analysis. Note the vastly improved agreement for the latter potential.

The initial RKR potential and the improved approximate potential are given in Table IV. Note the above mentioned shift in the region of the minimum. This shift is graphically presented in Fig. 2.

TABLE IV

POTENTIAL ENERGY CURVE FOR THE $X^2\Sigma^+$ STATE OF HgH[a]

r	RKR	IPA	r	RKR	IPA
1.45000	3637.143	3346.565	2.41343	2362.434	2341.610
1.46768	2952.797	2766.376	2.49466	2533.823	2551.343
1.47201	2801.110[b]	2637.285	2.55000		2660.602
1.48006	2533.823	2409.042	2.60000		2735.803
1.48554	2362.434	2262.022	2.65000		2785.992
1.49207	2168.580[c]	2094.931	2.71686	2801.110[b]	2815.806
1.49976	1954.106	1908.848	2.75000		2827.025
1.50875	1720.712	1704.550	2.80000		2839.000
1.51926	1469.953	1482.450	2.90000		2860.200
1.53125	1203.240[d]	1241.897	3.00000	2937.665	2877.000
1.54476	921.838	982.358	3.10000		2891.000
1.56002	626.871	703.503	3.20000		2902.500
1.57761	319.313	404.993	3.30000		2911.300
1.59906	0.000[e]	85.771	3.40000		2920.800
1.62899	- 330.382	- 258.362	3.50000	3008.787	2928.500
1.65241	- 499.547	- 444.790	3.60000		2935.500
1.67050	- 585.099	- 545.322	3.70000		2942.000
1.69938	- 657.455	- 641.504	3.80000		2948.400
1.71371	- 669.904	- 664.818	3.90000		2954.700
1.71841	- 671.149	- 669.406	4.00000	3025.343	2961.800
1.72281	- 671.149	- 672.437	4.10000		2969.000
1.72766	- 669.904	- 674.393	4.20000		2979.200
1.74349	- 657.455	- 671.395	4.30000		2985.000
1.78104	- 585.099	- 614.645	4.40000		2990.000
1.80923	- 499.547	- 534.476	4.50000	3029.995	2993.700
1.85219	- 330.382	- 364.625	4.60000		2997.600
1.91897	0.000[e]	- 20.034	4.70000		3000.500
1.97512	319.313	314.201	4.80000		3002.900
2.02633	626.871	632.165	4.90000		3005.900
2.07526	921.838	932.415	5.00000	3031.505	3007.700
2.12373	1203.240[d]	1214.781	5.10000		3009.800
2.17326	1469.953	1479.331	5.20000		3011.100
2.22534	1720.712	1725.868	5.30000		3012.700
2.28155	1954.106	1953.454	5.40000		3013.800
2.34351	2168.580[c]	2159.839	5.50000	3032.056	3014.800

[a] length in Å and energy in cm^{-1},

[b] $v = 3$,

[c] $v = 2$,
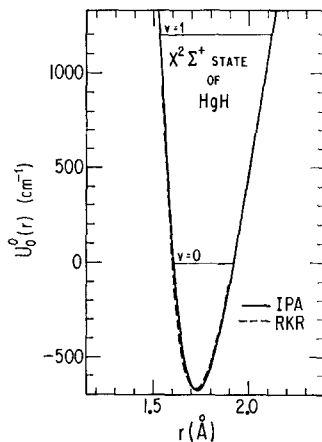
[d] $v = 1$,

[e] $v = 0$.

FIG. 2. The initial RKR (Rydberg–Klein–Rees) curve and the improved IPA (inverse perturbation analysis) curve in the region of the potential minimum.

It should be noted that the potential correction function, $\Delta U_0(r)$, is best determined in the region where the wavefunctions in Eqs. (9) are large. Thus $\Delta U_0(r)$ is dependent on the distribution of equations actually used in Eqs. (14). The equation for every observed vibrational–rotational term value need not be used, as long as there are more equations than unknown coefficients. But using only equations involving low vibrational states weights the system of equations so as to determine $\Delta U_0(r)$ only in the region of the potential minimum where the wave functions are large. Shifting the distribution to include higher vibrational states broadens the range over which $\Delta U_0(r)$ is a reliable correction. Beyond that range, $\Delta U_0(r)$ becomes poor as expected for a function expanded in a finite set of polynomial functions. Consequently, the long-range behavior for the improved approximate potential in Table IV is not determined well by the spectroscopic data available. We have chosen this long-range behavior to agree with that determined by Stwalley (13) from collisional data.

V. DISCUSSION

Recently there has been great interest in improving the accuracy of potential energy curve calculations. Two iterative potential curve improvement schemes have been proposed; one by Albritton, Harrop, Schmeltekopf, and Zare (14) and the other by Kirschner and Watson (15). Both iterate by using G_v and B_v expansions to determine the approximate potential by an RKR analysis and then use the approximate potential to correct the G_v and B_v expansions. Since both involve a semiclassical approximation in each iteration, whereas the inverse perturbation analysis proposed here is purely quantum mechanical within the iteration cycles, a direct comparison of these methods with the one proposed here is not entirely appropriate. In particular the method of Albritton et al., optimizing the data analysis itself, should be seen as complimentary to the IPA proposed here. However, it should be pointed out that the RKR procedure and the two iteration schemes mentioned above are specific to determining diatomic potential energy curves, whereas the inverse perturbation analysis given here is general and may be extended readily to potential energy surfaces using collision data or that from a spectroscopic normal coordinate analysis.

It should be noted, however, that the inverse perturbation analysis assumes the separation of electronic and nuclear motion; hence, it assumes that the adiabatic approximation is valid. If the adiabatic approximation breaks down, the inverse perturbation analysis will nevertheless attempt to find some potential curve which will satisfy the spectroscopic data within the adiabatic approximation, even though in these cases a potential for the nuclear motion has lost its physical meaning.

VI. CONCLUSION

In the test involving the known Davidson potential, the inverse perturbation analysis was shown to improve the accuracy of the approximating potential, vastly improving the agreement between the calculated and actual eigenvalues. In the application involving the $X^2\Sigma^+$ state of HgH, the inverse perturbation analysis was shown to improve the agreement between the calculated eigenvalues and the observed term values. The inverse perturbation analysis is thus demonstrated to be a viable technique for improving the accuracy of experimentally determined potential energy curves. In the case of HgH, it

is reasonable to assume that the final corrected potential is approaching the actual physical potential.

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