Comment on "Breakdown of the Hellmann-Feynman theorem: Degeneracy is the key"

R. Balawender and A. Holas
Institute of Physical Chemistry of the Polish Academy of Sciences, 44/52 Kasprzaka, 01-224 Warsaw, Poland

N. H. March
Department of Physics, University of Antwerp (RUCA), Groenenborgerlaan 171, B-2020 Antwerp, Belgium and University of Oxford, Oxford, England

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In a recent paper, Zhang and George [Phys. Rev. B **66**, 033110 (2002)] have made an application of the Hellmann-Feynman theorem (HFT) to calculate forces acting on an atom of the buckyball C_{60} when subjected to small displacement. They noticed inconsistent results (as compared with that by other method) for forces connected with states belonging to a degenerate-energy level. However a sum of all such HFT forces for a given level was found consistent. Therefore they proposed the average force to be the representative of all forces connected with a degenerate level. Our analysis of these difficulties, based on degenerate perturbation theory, leads to modification of the HFT in application to degenerate-level states. By solving a matrix eigenequation of the extended HFT, as many forces are obtained as degeneracy of the level amounts. The diagonalized matrix involves unperturbed states only. Our considerations are illustrated by a simple system—a particle moving in a harmonic confinement, where forces are connected with anisotropic deformation of an isotropic confinement.

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The Hellmann-Feynman theorem[1,2] (HFT) in its most basic form states that the expectation value (in the state Ψ_n) of the derivative of the Hamiltonian $H(\lambda)$, with respect to a parameter λ entering this Hamiltonian, is equal to $\partial E_n/\partial\lambda$, where $E_n(\lambda)$ is the eigenenergy of the state involved (interesting prehistory of the HFT is described by Gori-Giorgi and Ziesche[3] in their Ref. 41). In a recent paper, Zhang and George[4] (ZG) have made an application of the HFT to deal with the properties of the buckyball C_{60}. Namely, they calculated the force acting on a nucleus when subjected to small displacement. This force, specific for the ground state and each excited state separately of this C_{60} molecule, is defined as the derivative of the nth energy level with respect to the position vector of a nucleus, multiplied by (-1). Results obtained by means of the HFT have been compared with results from the direct finite-differential method computations. Finding discrepancies, sometimes very large, between these two approaches to obtain numerical estimates, ZG have traced this difficulty to degeneracy, and have claimed that for degenerate-level states there is a ''breakdown of the HFT,'' the forces are ''ill-defined.'' However, as they have observed, a sum of these ill-defined forces over all states, which belong to a degenerate level, is identical for both methods of calculations. So, the authors have proposed the average force of degenerate-level states to be a well-defined force characterizing this group of states.

The purpose of this Comment is to set out a first-principle approach, which is based on a quite general utilization of degenerate perturbation theory, to analyze and remove the difficulties which ZG[4] have encountered in the application of the HFT to degenerate states. It will be shown that there exist as many well-defined forces in connection with any degenerate energy level as its degeneracy amounts. The average of these forces equals to the average force introduced by ZG. Rather than attempting to pursue their example of C_{60}, for which their finite-differential results should be considered all correct and, therefore, solving their problem (however, outside the HFT scheme), we shall below give an example of a three-dimensional (3D) harmonic oscillator (HO), showing highly degenerate energy levels, which can largely be worked out analytically. We compare our six-fold degenerate level study with the highest (five-fold) degeneracy ZG encounter in their study of C_{60}.

With this background, we turn immediately to set out a first-principles approach to dealing with the ZG[4] problem of applying the HFT to such degenerate-energy states. We are going to adopt the Rayleigh-Schrödinger perturbation theory for the degenerate case (see, e.g., Ref. 5 or Ref. 6) to investigate the eigenequation of a Hamiltonian $H(\lambda)$,

$$H(\lambda)|\Psi_{j\alpha}(\lambda)\rangle = E_{j\alpha}(\lambda)|\Psi_{j\alpha}(\lambda)\rangle, \tag{1a}$$

$$\langle\Psi_{k\beta}(\lambda)|\Psi_{j\alpha}(\lambda)\rangle = \delta_{kj}\delta_{\beta\alpha}, \tag{1b}$$

in the vicinity of the zero value of the parameter λ. For this reason, the Hamiltonian is expanded in powers of λ,

$$H(\lambda) = H^{(0)} + \lambda H^{(1)} + \frac{1}{2}\lambda^2 H^{(2)} + \cdots, \tag{2}$$

$$H^{(k)} = \left(\frac{\partial}{\partial\lambda}\right)^k H(\lambda)|_{\lambda=0}, \quad k = 0,1,\ldots. \tag{3}$$

The notation of partial derivative is used to stress the fact, that, besides on λ, the Hamiltonian may depend on other parameters, which should be held fixed during the present considerations. The term $H^{(0)}$ of the expansion (2) will play the role of the unperturbed Hamiltonian, while $\lambda H^{(1)} + \mathcal{O}(\lambda^2)$—that of the perturbation. To handle conveniently degeneracies of the unperturbed problem, Eq. (1) at $\lambda = 0$,

$$H^{(0)}|\Psi_{j\alpha}^{(0)}\rangle = E_{j\alpha}^{(0)}|\Psi_{j\alpha}^{(0)}\rangle, \quad \langle\Psi_{k\beta}^{(0)}|\Psi_{j\alpha}^{(0)}\rangle = \delta_{kj}\delta_{\beta\alpha}, \tag{4}$$

a composed label $n=\{j,\alpha\}$ is introduced, such that α labels states of a d_j-fold degenerate level $E_j^{(0)}$,

$$E_{j\alpha}^{(0)} = E_j^{(0)} \quad \text{for } \alpha = 1,\ldots,d_j, \quad E_j^{(0)} < E_{j+1}^{(0)}. \tag{5}$$

Next, eigensolutions of Eq. (1) are expanded in powers of λ, similarly as the Hamiltonian in Eq. (2),

$$E_{j\alpha}(\lambda) = E_j^{(0)} + \lambda E_{j\alpha}^{(1)} + \mathcal{O}(\lambda^2), \tag{6a}$$

$$|\Psi_{j\alpha}(\lambda)\rangle = \sum_{\beta=1}^{d_j} |\Psi_{j\beta}^{(0)}\rangle U_{\beta\alpha}^{[j]} + \lambda|\Psi_{j\alpha}^{(1)}\rangle + \mathcal{O}(\lambda^2). \tag{6b}$$

Since, in the case of degeneracy, only whole d_j-dimensional subspace of eigenfunctions spanned by the basis $\{|\Psi_{j1}^{(0)}\rangle, |\Psi_{j2}^{(0)}\rangle, \ldots, |\Psi_{jd_j}^{(0)}\rangle\}$ (but not a separate function $|\Psi_{j\alpha}^{(0)}\rangle$) is determined uniquely, the 0th-order eigenfunction in Eq. (6b) is allowed to be a linear combination of the basis functions connected with the jth energy level. Orthonormality of these 0th-order eigenfunctions is assured by use of a $d_j \times d_j$ unitary matrix $U_{\beta\alpha}^{[j]}$,

$$\sum_{\beta=1}^{d_j} U_{\gamma\beta}^{[j]\dagger} U_{\beta\alpha}^{[j]} = \delta_{\gamma\alpha}. \tag{7}$$

After inserting the expansions (2) and (6) into Eq. (1a) we obtain from the terms $\propto\lambda^1$ the following equation:

$$(H^{(0)} - E_j^{(0)})|\Psi_{j\alpha}^{(1)}\rangle + (H^{(1)} - E_{j\alpha}^{(1)}) \sum_{\beta=1}^{d_j} |\Psi_{j\beta}^{(0)}\rangle U_{\beta\alpha}^{[j]} = 0. \tag{8}$$

This equation, when contracted with $\langle\Psi_{j\gamma}^{(0)}|$, simplifies, due to the conjugated Eq. (4) and Eq. (5), to

$$\sum_{\beta=1}^{d_j} \langle\Psi_{j\gamma}^{(0)}|H^{(1)}|\Psi_{j\beta}^{(0)}\rangle U_{\beta\alpha}^{[j]} = E_{j\alpha}^{(1)} U_{\gamma\alpha}^{[j]}. \tag{9}$$

Obtained equation represents a matrix eigenproblem in a d_j-dimensional space. It can be solved next for $\{E_{j\alpha}^{(1)}, \{U_{\gamma\alpha}^{[j]}, \gamma = 1,\ldots,d_j\}, \alpha = 1,\ldots,d_j\}$—the d_j eigenvalues and eigenvectors. This equation can be also rewritten in terms of the rotated 0th-order functions $|\tilde{\Psi}_{j\alpha}^{(0)}\rangle$ as

$$E_{j\alpha}^{(1)} = \langle\tilde{\Psi}_{j\alpha}^{(0)}|H^{(1)}|\tilde{\Psi}_{j\alpha}^{(0)}\rangle, \quad \alpha = 1,\ldots,d_j, \tag{10a}$$

where the matrix $U_{\beta\alpha}^{[j]}$ of the eigenvectors plays the role of the rotation matrix,

$$|\tilde{\Psi}_{j\alpha}^{(0)}\rangle = \sum_{\beta=1}^{d_j} |\Psi_{j\beta}^{(0)}\rangle U_{\beta\alpha}^{[j]}. \tag{10b}$$

The definition of a generalized force $F_{j\alpha}^{\lambda}$ connected with a displacement parameter λ and corresponding to the system in the state labeled by $n=\{j,\alpha\}$ is given by

$$F_{j\alpha}^{\lambda} = -\frac{\partial}{\partial\lambda} E_{j\alpha}(\lambda)|_{\lambda=0}. \tag{11a}$$

From Eq. (6a) we see immediately that

$$F_{j\alpha}^{\lambda} = -E_{j\alpha}^{(1)}, \tag{11b}$$

therefore Eqs. (9) and (10) solve the problem of determining this force. These equations provide an extension of the HFT to the degenerate level case.

Four conclusions, given below, represent the main result of our Comment: (i) there are d_j well-defined forces connected with the d_j-fold degenerate energy level $E_j^{(0)}$; (ii) the values of these forces can be obtained from the usual HFT formula

$$-\frac{\partial}{\partial\lambda} E_{j\alpha}(\lambda)|_{\lambda=0} = -\left\langle \tilde{\Psi}_{j\alpha}^{(0)} \middle| \left(\frac{\partial}{\partial\lambda} H(\lambda)\right)_{\lambda=0} \middle| \tilde{\Psi}_{j\alpha}^{(0)} \right\rangle, \tag{12}$$

provided the 0th-order eigenfunctions are constructed from the solutions $|\Psi_{j\beta}^{(0)}\rangle$ of the unperturbed problem (4) by means of rotations, Eq. (10b), where the matrix of eigenvectors of Eq. (9) plays the role of the rotation matrix $U_{\beta\alpha}^{[j]}$; (iii) alternatively, the forces can be determined from diagonalization of the $d_j \times d_j$ matrix

$$-\left\langle \Psi_{j\alpha}^{(0)} \middle| \left(\frac{\partial}{\partial\lambda} H(\lambda)\right)_{\lambda=0} \middle| \Psi_{j\beta}^{(0)} \right\rangle, \quad \alpha,\beta = 1,2,\ldots,d_j; \tag{13}$$

(iv) since diagonalization leaves the trace of a matrix invariant, from Eq. (9) follows

$$\frac{1}{d_j}\sum_{\alpha=1}^{d_j} F_{j\alpha}^{\lambda} = -\frac{1}{d_j}\sum_{\alpha=1}^{d_j} \left\langle \Psi_{j\alpha}^{(0)} \middle| \left(\frac{\partial}{\partial\lambda} H(\lambda)\right)_{\lambda=0} \middle| \Psi_{j\alpha}^{(0)} \right\rangle \tag{14}$$

[Eqs. (11b) and (3) were used too]—an analog of Eq. (10) in ZG.[4] The right-hand side of Eq. (14) represents an expression used by ZG to calculate the average force $\overline{F_j^{\lambda}}$—their only well-defined force corresponding to the degenerate level $E_j^{(0)}$. This force can be described as an average of ill-defined forces obtained by means of the usual HFT. The left-hand side of Eq. (14) represents a mean value of all forces corresponding to d_j states of the degenerate level $E_j^{(0)}$, which are determined by means of diagonalization of the matrix defined in Eq. (13). Thus Eq. (14) confirms that $\overline{F_j^{\lambda}}$ is really a well-defined force for the level $E_j^{(0)}$. However, it should be stressed that a well-defined force can be connected separately with each state $n=\{j,\alpha\}$ of this degenerate level $E_j^{(0)}$.

When calculated forces are used to do a molecular dynamics simulation, one may be tempted to apply in the case of d_j-fold degenerate level the single well-defined (average) force, Eq. (14), found and implicitly proposed for such use by ZG.[4] But there are d_j well-defined forces available in this case, all of the same importance. Therefore we propose either to branch simulation into d_j channels, each corresponding to one force, or to choose randomly one of the d_j forces with the probability $1/d_j$ for each. However, the reader should be cautioned that we are not specialists in the field of a simulation.

According to ZG[4] opinion, the forces given by the finite differential method themselves are not consistent. Let us investigate these forces in detail to see what is the actual meaning of such statement. We adopt the following definition for such a force—an analog of Eq. (4) of ZG[4]—

$$F_{j\alpha}^{\text{finite}}(\lambda)=-\frac{E_{j\alpha}^{\text{finite}}(\lambda)-E_{j\alpha}^{\text{finite}}(-\lambda)}{2\lambda}, \tag{15}$$

for some fixed λ satisfying $0<\lambda\ll\lambda_0=$ characteristic value. Here $E_{j\alpha}^{\text{finite}}(\lambda)$ is an eigenvalue of Eq. (1a); the corresponding eigenfunction is denoted as $|\Psi_{j\alpha}^{\text{finite}}(\lambda)\rangle$.

The definition of the state label $n=\{j,\alpha\}$ introduced by us earlier for the case of $\lambda=0$, Eq. (5), needs to be extended now to the case of $\lambda\neq 0$, for use in Eq. (15). When $|\lambda|$ is small enough, the spectrum of eigenvalues of Eq. (1a) resembles the spectrum of Eq. (4), but with the level $E_j^{(0)}$ split into no more than d_j sublevels, close to $E_j^{(0)}$ (degeneracies are not excluded). Let labeling of states, connected with these sublevels, by $n=\{j,\alpha\}$, $\alpha=1,2,\ldots,d_j$, be such that inequalities for eigenenergies

$$E_{j\alpha}^{\text{finite}}(\lambda)\leqslant E_{j(\alpha+1)}^{\text{finite}}(\lambda),\quad E_{j\alpha}^{\text{finite}}(-\lambda)\geqslant E_{j(\alpha+1)}^{\text{finite}}(-\lambda), \tag{16}$$

are satisfied (here $\lambda>0$). We are ready now to relate the finite-λ eigensolution $E_{j\alpha}^{\text{finite}}(\lambda)$, $|\Psi_{j\alpha}^{\text{finite}}(\lambda)\rangle$ with the solution $E_{j\alpha}(\lambda)$, $|\Psi_{j\alpha}(\lambda)\rangle$, Eq. (6), obtained by means of the perturbation theory. The first-order energy term and the 0th-order wave function term in Eq. (6) are given in Eq. (10) in terms of the solution of Eq. (9). It will be convenient to change the order of labels α there to have $E_{j\alpha}^{(1)}\leqslant E_{j(\alpha+1)}^{(1)}$ satisfied. Then, because both methods of solving Eq. (1a) should lead to equivalent results, we find

$$E_{j\alpha}^{\text{finite}}(\lambda)=E_j^{(0)}+\lambda E_{j\alpha}^{(1)}+\mathcal{O}(\lambda^2),\quad \alpha=1,2,\ldots,d_j, \tag{17}$$

for energy. The corresponding relations for wave functions should take into account possible degeneracies of the first-order term $E_{j\alpha}^{(1)}$ in the expansion (17). Thus, in the case of d-fold degeneracy of the energy *derivative* $E_{j(\alpha+\beta)}^{(1)}$,

$$E_{j\alpha}^{(1)}<E_{j(\alpha+1)}^{(1)}=\cdots=E_{j(\alpha+d)}^{(1)}<E_{j(\alpha+d+1)}^{(1)}, \tag{18a}$$

$d\leqslant d_j$, the d-dimensional subspaces of functions from two methods are equivalent, separately for solutions at λ positive and negative,

$$|\Psi_{j(\alpha+\beta)}^{\text{finite}}(\pm\lambda)\rangle=\sum_{\gamma=1}^{d}|\tilde{\Psi}_{j(\alpha+\gamma)}^{(0)}\rangle U_{\gamma\beta}^{[\pm]}+\mathcal{O}(\lambda), \tag{18b}$$

for $\beta=1,\ldots,d$, where $U_{\gamma\beta}^{[+]}$ and $U_{\gamma\beta}^{[-]}$ are some $d\times d$ unitary matrices. In particular, for a nondegenerate case, $d=1$, $|U_{11}^{[+]}|=|U_{11}^{[-]}|=1$. After substituting $E_{j\alpha}^{\text{finite}}(\lambda)$ from Eq. (17) into Eq. (15) we find

$$F_{j\alpha}^{\text{finite}}(\lambda)=-E_{j\alpha}^{(1)}+\mathcal{O}(\lambda),\quad \text{for}\ \ \alpha=1,2,\ldots,d_j. \tag{19}$$

From comparison of this result with that of Eq. (11b) we conclude that forces given by the finite-differential method are consistent with forces given by the present perturbation-theory extension of the HFT. However they are inconsistent with the ill-defined HFT forces [the diagonal elements of the force matrix, Eq. (13)], which have been discussed by ZG[4] and shown in their Table I.

To illustrate the above considerations, we are going to consider a very simple system—a particle moving in a harmonic confinement. Experiments on ultracold vapors of ^{40}K and ^{6}Li isotopes populating hyperfine states inside magnetic traps (see, e.g., Refs. 7 and 8 and references therein) have motivated renewed theoretical studies on harmonic confinement. Indeed, in current experimental approaches, using axially symmetric magnetic traps, it proves possible to range from a quasi-1D trap through a quasi-2D trap, to a fully spherical 3D trap. This has provided the stimulation for us to use a related example in the present HFT context, in studying perturbations from an isotropic 3D HO. Our system consists of one particle of mass m_0, coordinate $\mathbf{r}=(r_1,r_2,r_3)$, moving in a harmonic confinement defined by three characteristic energies $\hbar\omega_i$, $i=1,2,3$, or, equivalently, spring constants $k_i=m_0\omega_i^2$. The corresponding Hamiltonian is

$$H=\sum_{i=1}^{3}\left[-\frac{\hbar^2}{2m_0}\left(\frac{\partial}{\partial r_i}\right)^2+\frac{1}{2}k_i r_i^2\right]. \tag{20}$$

Because of numerous degeneracies of its energy levels, isotropic confinement (of characteristic energy $\hbar\omega_0$) is chosen for an unperturbed system. With force constants parametrized as

$$k_3=m_0\omega_0^2,\quad k_1=(1+\lambda\cos^2(\kappa))k_3,$$
$$k_2=(1+\lambda\sin^2(\kappa))k_3, \tag{21}$$

these degeneracies diminish or disappear for $\lambda\neq 0$, details depend on κ. While in their C_{60} example ZG[4] calculated forces connected with displacement of an atom, forces in our example will be connected with modifications of spring constants of the confining potential, caused by $\lambda\neq 0$.

In units of $a_0=\sqrt{\hbar/(m_0\omega_0)}$ for length and $\hbar\omega_0$ for energy, the Hamiltonian depends on two parameters only, $H=H(\lambda,\kappa)$. As a function of κ, it is periodic and symmetric, $H(\lambda,\kappa+\pi)=H(\lambda,\kappa)=H(\lambda,-\kappa)$. The terms $H^{(k)}$, Eq. (3), of the expansion (2) are

$$H^{(0)}=-\frac{1}{2}\nabla^2+\frac{1}{2}r^2, \tag{22a}$$

$$H^{(1)}=\frac{1}{2}(\cos^2(\kappa)r_1^2+\sin^2(\kappa)r_2^2), \tag{22b}$$

$H^{(k)}=0$ for $k\geqslant 2$. The solutions of the unperturbed problem—the 3D isotropic HO—are known (see, e.g., Ref. 9): for $\nu=0,1,2,\ldots$—the radial quantum number, $l=0,1,2,\ldots$—the orbital momentum one, and $m=-l,-l+1,\ldots,l$—the spatial magnetic one,

$$E_{\nu lm}^{(0)}=\frac{3}{2}+2\nu+l, \tag{23a}$$

$$\Psi^{(0)}_{\nu lm}(\mathbf{r}) = u_{\nu l}(r) Y_{lm}(\theta,\phi), \tag{23b}$$

where $\mathbf{r}=(\sin(\theta)\cos(\phi),\sin(\theta)\sin(\phi),\cos(\theta))r$, Y_{lm} is the spherical harmonic [the definition (7.34) in Ref. 6 is used here], the radial function $u_{\nu l}$ is given in terms of a confluent hypergeometric function; two functions to be used in our example are

$$u_{10}(r) = 6^{1/2}\pi^{-1/4}\left(1-\frac{2}{3}r^2\right)\exp\left(-\frac{1}{2}r^2\right), \tag{23c}$$

$$u_{02}(r) = 15^{-1/2}\pi^{-1/4}4r^2\exp\left(-\frac{1}{2}r^2\right). \tag{23d}$$

As follows from Eq. (23a), energy levels can be expressed as $E^{(0)}_j = \frac{3}{2}+j$, $j=0,1,\ldots$ [see Eq. (5)], while the decomposition of j into $2\nu+l$ with various pairs $\{\nu,l\}$ and $(2l+1)$ values of m lead to degeneracies: $d_0=1$, $d_1=3$, $d_2=6$, $d_3=10$, and so on. As an illustrative example in our Comment, the six-fold degenerate level $E^{(0)}_{j=2}$ is chosen, with the following correspondences $\{j\alpha\}\Leftrightarrow\{\nu lm\}$ between labeling: $\{21\}\Leftrightarrow\{100\}$, $\{22\}\Leftrightarrow\{02\overline{2}\}$, $\{23\}\Leftrightarrow\{02\overline{1}\}$, $\{24\}\Leftrightarrow\{020\}$, $\{25\}\Leftrightarrow\{021\}$, $\{26\}\Leftrightarrow\{022\}$. To calculate forces corresponding to this level, which are connected with λ, by applying Eqs. (11b) and (9), the following matrix needs to be evaluated: $H^{(1)}_{\alpha\beta}=\langle 2\alpha|H^{(1)}|2\beta\rangle$, where $|2\beta\rangle = |\Psi^{(0)}_{2\beta}\rangle$. According to Eq. (22b), it can be decomposed as

$$H^{(1)}_{\alpha\beta}(\kappa) = \frac{1}{2}(\cos^2(\kappa)C_{\alpha\beta}+\sin^2(\kappa)S_{\alpha\beta}), \tag{24a}$$

in terms of Hermitian matrices

$$C_{\alpha\beta} = \langle 2\alpha|r^2\sin^2(\theta)\cos^2(\phi)|2\beta\rangle, \tag{24b}$$

$$S_{\alpha\beta} = \langle 2\alpha|r^2\sin^2(\theta)\sin^2(\phi)|2\beta\rangle. \tag{24c}$$

The matrix elements $C_{\alpha\beta}$ and $S_{\alpha\beta}$ are evaluated analytically: while integrations over r and ϕ are elementary, that over θ are reduced to orthogonality relations between the spherical harmonics due to an identity quoted in Eq. (61.7) of Ref. 9,

$$\cos(\theta)Y_{lm}(\theta,\phi) = \beta_{l+1,m}Y_{l+1,m}(\theta,\phi)+\beta_{lm}Y_{l-1,m}(\theta,\phi), \tag{25a}$$

$$\beta_{lm} = \sqrt{(l^2-m^2)/(4l^2-1)}, \tag{25b}$$

applied to $\sin^2(\theta)Y_{lm}(\theta,\phi)=(1-\cos^2(\theta))Y_{lm}(\theta,\phi)$ twice. The following real-valued result is obtained,

$$\begin{gathered} C_{11}=S_{11}=7/6, \quad C_{44}=S_{44}=5/6, \\ C_{22}=S_{22}=C_{66}=S_{66}=3/2, \\ C_{33}=S_{33}=C_{55}=S_{55}=1, \\ S_{12}=-C_{12}=S_{16}=-C_{16}=1/\sqrt{3}, \\ S_{24}=-C_{24}=S_{46}=-C_{46}=1/\sqrt{6}, \\ S_{35}=-C_{35}=1/2, \quad S_{14}=+C_{14}=\sqrt{2}/3, \end{gathered} \tag{26}$$

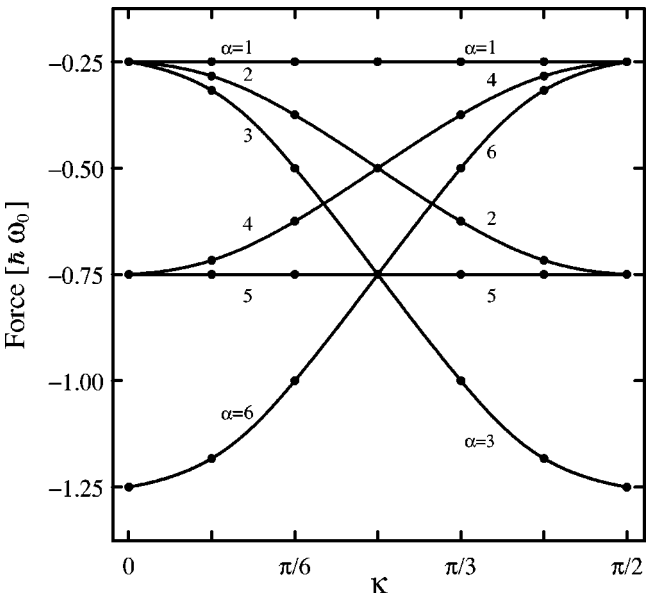

FIG. 1. Forces connected with the six-fold degenerate level $E^{(0)}_2$ vs. κ: points, $F^{\lambda}_{2\alpha}(\kappa)$ from diagonalizing the matrix, $H^{(1)}_{\alpha\beta}(\kappa)$; lines, $F^{\text{finite}}_{2\alpha}(0,\kappa)$ from energy levels obtained at finite λ.

$$S_{\alpha\beta}=C_{\alpha\beta}=0 \quad \text{for remaining} \quad \alpha\beta.$$

Calculated forces—eigenvalues of $-H^{(1)}_{\alpha\beta}(\kappa)$, for some chosen κ (from its irreducible range $[0,\pi/2]$), are shown in Fig. 1 as points. While for a general κ there are six different forces, for $\kappa=0$, $\pi/4$ and $\pi/2$ there are three different forces only: a triple-degenerate, double-degenerate, and nondegenerate one. Similar structure was obtained by ZG[4] for the five-fold degenerate energy level E_n, $n=14,15,\ldots,18$ of C_{60}, for the finite-differential forces, namely, a triple-degenerate force F_n, $n=15,16,17$, and two forces, $n=14,18$, almost degenerate.

Since our model Hamiltonian, Eq. (20), is a sum of three different 1D HO Hamiltonians $H_i(r_i)$, the eigensolutions of Eq. (1) for arbitrary, finite λ and κ can be written as a combination of the solutions of the 1D HO problem,

$$E^{\text{HO}}_n(\hbar\omega) = \left(\frac{1}{2}+n\right)\hbar\omega, \tag{27a}$$

$$\Psi^{\text{HO}}_n(x;a) = c_n a^{-1/2}H_n(x/a)\exp\left(-\frac{1}{2}(x/a)^2\right) \tag{27b}$$

[$H_n(\xi)$—the Hermite polynomial], namely, for $n_i=0,1,\ldots,$—the ith oscillator quantum number, $i=1,2,3$,

$$\begin{aligned} E^{\text{finite}}_{n_1n_2n_3}(\lambda,\kappa) = {} & E^{\text{HO}}_{n_1}((1+\lambda\cos^2(\kappa))^{1/2}) \\ & + E^{\text{HO}}_{n_2}((1+\lambda\sin^2(\kappa))^{1/2}) + E^{\text{HO}}_{n_3}(1), \end{aligned} \tag{28a}$$

$$\Psi^{\text{finite}}_{n_1 n_2 n_3}(\mathbf{r};\lambda,\kappa) = \Psi^{\text{HO}}_{n_1}(r_1;(1+\lambda\cos^2(\kappa))^{-1/4}) \times \Psi^{\text{HO}}_{n_2}(r_2;(1+\lambda\sin^2(\kappa))^{-1/4})\Psi^{\text{HO}}_{n_3}(r_3;1) \quad (28b)$$

(units as previously). With the correspondences $\{j\alpha\}\Leftrightarrow\{n_1 n_2 n_3\}$ between labeling: $\{21\}\Leftrightarrow\{002\}$, $\{22\}\Leftrightarrow\{011\}$, $\{23\}\Leftrightarrow\{020\}$, $\{24\}\Leftrightarrow\{101\}$, $\{25\}\Leftrightarrow\{110\}$, $\{26\}\Leftrightarrow\{200\}$, the unperturbed six-fold degenerate level is $E^{\text{finite}}_{2\alpha}(\lambda=0,\kappa)=E^{\text{finite}}_{n_1 n_2 n_3}(0,\kappa)=E^{(0)}_2=7/2$, while the ordering shown in Eq. (16) is satisfied for small λ when $\kappa\lesssim 0.6$

Since the dependence of the energy on λ is known from Eq. (28a) in analytical form, the corresponding force can be determined also in the limit of $\lambda\to 0$ to be

$$F^{\text{finite}}_{j\alpha}(0,\kappa) = F^{\text{finite}}_{n_1 n_2 n_3}(0,\kappa) = -\frac{\partial}{\partial\lambda}E^{\text{finite}}_{n_1 n_2 n_3}(\lambda,\kappa)\big|_{\lambda=0} = -\frac{1}{2}\left(\left(\frac{1}{2}+n_1\right)\cos^2(\kappa)+\left(\frac{1}{2}+n_2\right)\sin^2(\kappa)\right). \quad (29)$$

These forces $F^{\text{finite}}_{j\alpha}(0,\kappa)$ for $\alpha=1,2,\ldots,6$ are plotted in Fig. 1 as continuous lines. The points, which represent forces determined by the extended HFT, lay exactly on the lines.

To illustrate equivalence of wave functions obtained by two methods, Eq. (18b), let us take for $\kappa=0$ the double-degenerate energy derivative $E^{(1)}_{23}<E^{(1)}_{24}=E^{(1)}_{25}<E^{(1)}_{26}$ [compare Eq. (18a), see the corresponding forces equal to $-0.75\hbar\omega_0$ in Fig. 1]. The 2×2 matrix $U_{\gamma\beta}$ is evaluated from $\langle\tilde{\Psi}^{(0)}_{2(3+\gamma)}|\Psi^{\text{finite}}_{2(3+\beta)}\rangle$, in the limit of $\lambda\to 0$. Since the dependence on λ is known from Eq. (28b) in analytical form, the same U is determined for positive and negative λ. The following values are obtained $U_{11}=-p$, $U_{22}=-ip$, $U_{12}=-iq$, $U_{21}=q$ where $p=0.997\,67$, $q=0.068\,19$. Such matrix is unitary, as expected.

In concluding, the results of our example show that forces and states obtained from the extended HFT [Eqs. (9)–(11) and a summary below these equations] are consistent with results stemming from the exact solutions for arbitrary λ.

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