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LETTER TO THE EDITOR

# The Born–Oppenheimer electric gauge force is repulsive near degeneracies

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**Abstract.** The Born-Oppenheimer approximation implies gauge potentials of electric and magnetic type in the Hamiltonian governing the slow part of the system. Here we demonstrate that the electric gauge potential is repulsive near points in the space of slow parameters at which energies of the fast system are degenerate. The repulsion is an inverse-cube force.

It has recently been appreciated [1-3] that conventional Born-Oppenheimer theory leads to the appearance of gauge potentials of electric and magnetic type in the effective Hamiltonian for the slow system, in addition to the familiar potential-energy surface from the fast eigenvalues. Here we describe a curious feature of the electric gauge force. This has been mentioned before [4], but now we give a more detailed account.

The fast system is described by a set of dynamical variables (coordinates, momenta, spins) represented by $\hat{\xi}$ and the slow system by coordinates $X$ and conjugate momentum operators $\hat{P}$. We may cast the Hamiltonian of the entire system in the general form

$$\hat{H} = \tfrac{1}{2}\sum_{ij} Q_{ij}\hat{P}_i\hat{P}_j + \hat{H}_f(\hat{\xi}; X) \tag{1}$$

where $\hat{H}_f$ is the Hamiltonian for the fast system and includes the potential energy of interaction with and within the slow part. The first term represents the kinetic energy of the slow system, with $Q_{ij}$ being an inverse mass tensor. In the simplest case where the slow particles all have the same mass $M$, $Q_{ij}$ is clearly the identity matrix of appropriate size, divided by $M$. When the particles have different masses, $Q_{ij}$ is diagonal in Cartesian coordinates. Obviously $Q_{ij}$ is positive definite; this will be crucial.

Let the fast system be in the $n$th eigenstate $|n(X)\rangle$ of $\hat{H}_f$ with energy $E_n(X)$. In the Born-Oppenheimer approximation we take the state of the entire system to be of the separable form $|n(X)\rangle\Psi_s(X)$, where $\Psi_s(X)$ is the wavefunction of the slow system, in which (here and hereafter) we suppress an obvious $n$ dependence. The effective Hamiltonian governing $\Psi_s$ is $\hat{H}_{\mathrm{eff}} \equiv \langle n|\hat{H}|n\rangle$. It is then easy to show, using $\hat{P}_i \equiv -\mathrm{i}\hbar\partial/\partial X_i \equiv -\mathrm{i}\hbar\partial_i$, that

$$\hat{H}_{\mathrm{eff}} = \tfrac{1}{2}\sum_{ij} Q_{ij}\{\hat{P}_i - A_i\}\{\hat{P}_j - A_j\} + \Phi + E_n \tag{2}$$

where the magnetic vector and electric scalar gauge potentials $A_i$ and $\Phi$ are

$$A_i(X) = \mathrm{i}\hbar\langle n|\partial_i n\rangle \tag{3}$$

and

$$\Phi(X) = \frac{\hbar^2}{2}\sum_{ij} Q_{ij} g_{ij}(X) \tag{4}$$

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with

$$g_{ij}(X) = \mathrm{Re}[\langle \partial_i n|(1-|n\rangle\langle n|)|\partial_j n\rangle] \tag{5}$$

($g_{ij}$ is in fact the quantum metric tensor [4, 5]). In a cycle of the slow parameters $X$, the integral of the vector potential gives the familiar geometric phase.

We now show that the pseudo-electric gauge potential $\Phi$ is inverse square and repulsive close to points in the space of slow parameters that correspond to degeneracies in $E_n(X)$, provided the inverse mass tensor has positive eigenvalues. Near a degeneracy it is the adjacent states which dominate $g_{ij}$. To see why, rewrite (5) in the form

$$g_{ij} = \mathrm{Re}\left[\sum_{m\neq n} \langle \partial_i n|m\rangle\langle m|\partial_j n\rangle\right] \tag{6}$$

using the resolution of the identity. Since

$$\langle m|\partial_i n\rangle = \frac{\langle m|\partial_i \hat{H}_f|n\rangle}{E_n - E_m} \tag{7}$$

(obtained by differentiating the eigenequation), it is the state $|m=n+1\rangle$ or $|m=n-1\rangle$ which becomes important close to a degeneracy.

Consider therefore the simplest case of a two-state fast system, and take (without essential loss of generality) $\hat{H}_f = \boldsymbol{\sigma}\cdot\boldsymbol{X}$ where $\boldsymbol{\sigma}$ is a vector whose components are the Pauli spin matrices and $\boldsymbol{X} \equiv (X_1, X_2, X_3)$ is a position vector in the three-dimensional space of relevant slow parameters. For convenience we shall use Cartesian coordinates.

We now need $g_{ij}$ for this model. Recall that the $|n\rangle$ represent eigenstates of $\hat{H}_f$. The operator has two eigenstates which we denote $|+\rangle$ and $|-\rangle$, satisfying $\hat{H}_f|\pm\rangle = \pm X|\pm\rangle$ with $X \equiv |\boldsymbol{X}|$. The degeneracy is thus at the origin of $\boldsymbol{X}$ space. Differentiating this eigenequation with respect to $X_i$ leads to

$$(\boldsymbol{\sigma}\cdot\boldsymbol{X})|\partial_i \pm\rangle + (\boldsymbol{\sigma}\cdot\boldsymbol{e}_i)|\pm\rangle = \pm[(\boldsymbol{e}_i\cdot\boldsymbol{x})|\pm\rangle + X|\partial_i \pm\rangle] \tag{8}$$

where $\boldsymbol{x} \equiv \boldsymbol{X}/X \equiv (x_1, x_2, x_3)$ and $\boldsymbol{e}_i$ is the unit vector in the direction of the $i$th coordinate. We thus have

$$\langle \mp|\boldsymbol{\sigma}\cdot\boldsymbol{e}_i|\pm\rangle = \pm 2X\langle \mp|\partial_i \pm\rangle. \tag{9}$$

If the fast system is in the $|+\rangle$ state, we have, from (6),

$$g_{ij} = \mathrm{Re}[\langle \partial_i +|-\rangle\langle -|\partial_j +\rangle] = \frac{1}{4X^2}\mathrm{Re}[\langle -|\boldsymbol{\sigma}\cdot\boldsymbol{e}_i|+\rangle\langle +|\boldsymbol{\sigma}\cdot\boldsymbol{e}_j|-\rangle]. \tag{10}$$

The trick is to go now to rotated axes such that the $x_3$ direction coincides with $\boldsymbol{X}$. Then since only the off-diagonal elements of the Pauli matrices appear in (10), we need only look at contributions from $\sigma_1$ and $\sigma_2$. It is now a straightforward exercise to show that the RHS of (10) equals

$$\frac{1}{4X^2}[(\boldsymbol{e}_i\cdot\boldsymbol{e}_1)(\boldsymbol{e}_j\cdot\boldsymbol{e}_1) + (\boldsymbol{e}_i\cdot\boldsymbol{e}_2)(\boldsymbol{e}_j\cdot\boldsymbol{e}_2)] \tag{11}$$

which, upon reverting to the original coordinate axes, gives

$$g_{ij} = \frac{1}{4X^2}[\boldsymbol{e}_i\cdot\boldsymbol{e}_j - (\boldsymbol{e}_i\cdot\boldsymbol{x})(\boldsymbol{e}_j\cdot\boldsymbol{x})]. \tag{12}$$

If the fast system is in the $|-\rangle$ state, $g_{ij}$ is given by the same expression (there is no minus sign).

$g_{ij}$ has one zero eigenvalue and one doubly-degenerate eigenvalue and so diagonalises to

$$\frac{1}{4X^2}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{13}$$

In this frame only the diagonal terms of $Q_{ij}$ contribute to the summation in (4). Let $P_{ij}$ be an orthogonal rotation matrix needed to get from the Cartesian frame in which $Q$ is diagonal to one which diagonalises $g_{ij}$. In the latter frame, the diagonal terms of $Q$ are easily shown to be of the form $Q_{ii} = \Sigma_j q_j P_{ji}^2$, where the $q_j$ are the eigenvalues of $Q$. Thus, because the inverse mass tensor has only positive eigenvalues, its diagonal elements will be positive in any rotated coordinate system, and (4) is positive. So we have an electric gauge potential that, in the vicinity of degeneracies in $E_n(X)$, is inverse square in the distance from the degeneracy and also positive. Therefore there is an inverse-cube repulsive gauge force centred on the degeneracy, as claimed.

In applications of Born–Oppenheimer theory (e.g. to molecules), it is common to treat the slow system semiclassically as well as adiabatically, because this system is heavy as well as slow. Then the $\hbar$-dependence of the gauge potentials becomes important. The magnetic potential $A_i$ is proportional to $\hbar$ and so is comparable with energy spacings of one-dimensional (e.g. WKB) subsequences of vibronic levels. Therefore it gives appreciable contributions to such levels [6].

The electric potential $\Phi$ is proportional to $\hbar^2$ and so gives negligible semiclassical contributions to one-dimensional subsequences. It will, however, have two other effects. First, it will give appreciable contributions to level sequences corresponding to chaotic nuclear motion, because the spacing is now $\hbar^N$ where $N$, the number of relevant freedoms, is at least 2. Second, because of the result demonstrated here, $\Phi$ cannot be ignored near a degeneracy, because of the singularity there. Its effect will be to improve the adiabatic approximation by repelling the slow system from degeneracies and so reducing the probability of non-adiabatic transitions between fast states $|n\rangle$.

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