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Relationes

Spectral Variational Principle for Green's Functions

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For a suitable approximation $\tilde{K}(q, q', \tau)$ to the Dirac-Feynman Green's function of a quantum-mechanical system, the parameter $\Delta \equiv \mathrm{tr}[\mathcal{S}\tilde{K} \cdot (\mathcal{S}\tilde{K})^*]$ is defined, where $\mathcal{S} \equiv i\partial/\partial\tau - \mathcal{H}$. It is shown that $\Delta \geqq 0$ and $\Delta \to 0$ as $\tilde{K} \to K$, the exact Green's function, thus providing a criterion on approximate Green's functions analogous in its role to the variational principle for wavefunctions. A second somewhat weaker criterion is also proposed, based on $\Sigma \equiv [\mathrm{tr}\,\tilde{K}^*\,\mathrm{tr}\,\mathcal{S}^2\tilde{K} - |\mathrm{tr}\,\mathcal{S}\tilde{K}|^2]_{\tau\,\mathrm{avg}} \geqq 0$. Recipes are given for projecting out continuum contributions to Δ or Σ and for analyzing for the discrete eigenvalue spectrum.

Um zu Näherungen $\tilde{K}(q, q', \tau)$ für die Dirac-Feynman-Greensche Funktion eines quantenmechanischen Systems zu gelangen, wird der Parameter $\Delta \equiv \mathrm{tr}[\mathcal{S}\tilde{K} \cdot (\mathcal{S}\tilde{K})^*]$ definiert, wobei $\mathcal{S}$ für $i\partial/\partial\tau - \mathcal{H}$ steht. Es wird gezeigt, daß $\Delta \geqq 0$ und $\Delta \to 0$ wenn $\tilde{K} \to K$, so daß damit ein Kriterium für Näherungen der Green'schen Funktion analog dem Variationsprinzip für Wellenfunktionen gefunden ist. Als zweites, wenn auch schwächeres Kriterium gründet sich auf

$$\Sigma \equiv [\mathrm{tr}\,\tilde{K}^*\,\mathrm{tr}\,\mathcal{S}^2\tilde{K} - |\mathrm{tr}\,\mathcal{S}\tilde{K}|^2]_{\tau\,\mathrm{avg}} \geqq 0\,.$$

Hinweise für das Herausprojizieren der Beträge des Kontinuums aus Δ bzw. Σ und für die Analyse des diskreten Spektrums werden gegeben.

1. Properties of Exact Green's Functions

The Dirac-Feynman Green's function or propagator for a quantum-mechanical system is given by

$$K(q, q', \tau) \equiv \langle q' t' | q t \rangle = \langle q' | \mathcal{T}(\tau) | q \rangle\,, \tag{1}$$

where $\tau = t - t'$. For time-independent Hamiltonian, the evolution operator takes the simple form

$$\mathcal{T}(\tau) = e^{-i\tau\mathcal{H}} \tag{2}$$

so that the Green's function has the following spectral representation in terms of the energy eigenstates:

$$K(q, q', \tau) = \sum_n \psi_n(q)\, \psi_n^*(q')\, e^{-i\omega_n\tau}\,. \tag{3}$$

In principle therefore, if K is known, the complete spectrum of eigenstates is accessible by fourier analysis [1].

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The Green's function is a solution of the time-dependent Schrödinger equation in both unprimed and primed coordinates:

$$\mathcal{S}\, K(q, q', \tau) = \mathcal{S}'^{\dagger} K(q, q', \tau) = 0 \tag{4}$$

with the initial condition

$$K(q, q', 0) = \delta(q - q') . \tag{5}$$

For convenience, we have defined the "Schrödinger operator"

$$\mathcal{S} \equiv i\frac{\partial}{\partial t} - \mathcal{H} = i\frac{\partial}{\partial \tau} - \mathcal{H} . \tag{6}$$

Accordingly, $\mathcal{S}' = i\partial/\partial t' - \mathcal{H}' = -i\partial/\partial\tau - \mathcal{H}'$ and $\mathcal{S}'^{\dagger} = i\partial/\partial\tau - \mathcal{H}'$. We note, incidentally, that $K(q, q', \tau)$ is technically the Green's function for the inverse evolution operator, i.e.

$$\mathcal{T}^{\dagger}(\tau)\, K(q, q', \tau) = \delta(q - q') . \tag{7}$$

Better known in the quantum theory of scattering are time-dependent Green's functions which are solutions of

$$\mathcal{S}\, G(q, q', \tau) = \delta(\tau)\, \delta(q - q') . \tag{8}$$

These are evidently related to K as follows:

$$\begin{aligned} G_{\text{ret}}(q, q', \tau) &= -i\Theta(\tau)\, K(q, q', \tau) , \\ \text{or} \qquad G_{\text{adv}}(q, q', \tau) &= i\Theta(-\tau)\, K(q, q', \tau) , \end{aligned} \tag{9}$$

where $\Theta(\tau)$ is the unit step function. Conversely,

$$K(q, q', \tau) = i[G_{\text{ret}}(q, q', \tau) - G_{\text{adv}}(q, q', \tau)] . \tag{10}$$

2. Approximate Green's Functions

Supposing the exact Green's function for a particular quantum system to be unavailable, we should like to deal with approximation functions $\tilde{K}(q, q', \tau)$ with a view toward extracting approximate eigenvalues and eigenfunctions. Primarily, we shall focus on the discrete eigenvalue spectrum.

Accordingly, let an otherwise arbitrary function $\tilde{K}(q, q', \tau)$ conform to the following conditions (which all apply to exact Green's functions):

i) $\tilde{K}(q, q', \tau)$ obeys the same analyticity, continuity, boundary, permutation and symmetry conditions as are appropriate to $K(q, q', \tau)$.

ii) $\tilde{K}^*(q, q', \tau) = \tilde{K}(q', q, -\tau)$.

iii) $\tilde{K}(q, q'', \tau_1) \cdot \tilde{K}(q'', q', \tau_2) = \tilde{K}(q, q', \tau_1 + \tau_2)$, scalar product signifying integration over q''.

iv) $\tilde{K}(q, q', 0) = \delta(q - q')$.

As shown in the Appendix, conformity with (i)–(iv) specifies a function possessing the formal structure

$$\tilde{K}(q, q', \tau) = \sum_n \phi_n(q)\, \phi_n^*(q')\, e^{-i\lambda_n \tau} \tag{11}$$

in which $\{\phi_n(q)\}$ represents some complete orthonormal set spanning the same function space as the eigenfunctions $\{\psi_n(q)\}$ and $\{\lambda_n\}$ is some associated set of real numbers.

Presuming that $\mathscr{S}\tilde{K} \neq 0$, so that $\tilde{K}$ is not the exact Green's function, define the parameter

$$\Delta \equiv \operatorname{tr}[\mathscr{S}\tilde{K} \cdot (\mathscr{S}\tilde{K})^*] . \tag{12}$$

By writing this in the redundant form

$$\Delta = \operatorname{tr}[\tilde{K}^* \cdot \mathscr{S}\tilde{K} \cdot (\mathscr{S}\tilde{K})^* \cdot \tilde{K}] \tag{13}$$

it follows most directly that Δ has the formal structure

$$\Delta = \sum_m \sum_n |\lambda_n \delta_{mn} - H_{mn}|^2 \tag{14}$$

with

$$H_{mn} \equiv (\phi_m, \mathscr{H} \phi_n) . \tag{15}$$

By reduction of (14), or directly from (12), we find alternatively

$$\Delta = \sum_n [\lambda_n^2 - 2\lambda_n H_{nn} + (H^2)_{nn}] = \sum_n [(\lambda_n - H_{nn})^2 + \sigma_n^2] , \tag{16}$$

where each σ_n represents an energy variance, i.e.

$$\sigma_n^2 \equiv (H^2)_{nn} - (H_{nn})^2 = (\phi_n, [\mathscr{H} - H_{nn}]^2 \phi_n) \geqq 0 . \tag{17}$$

Equivalent forms for Δ, as suggested by (16), are

$$\Delta = \operatorname{tr} \mathscr{S}^2 \tilde{K}|_{\tau=0} = [\operatorname{tr} \tilde{K}^* \operatorname{tr} \mathscr{S}^2 \tilde{K}]_{\tau \mathrm{avg}} \tag{18}$$

and, in any case,

$$\Delta \geqq 0 . \tag{19}$$

The summation (14) runs over the elements of the infinite secular determinant for the Hamiltonian in the basis $\{\phi_n(q)\}$. Clearly, Δ can vanish only if $\{\phi_n\}$ diagonalizes $\mathscr{H}$, which means that $\phi_n = \psi_n$, $\lambda_n = \omega_n$, for all n. Alternatively, from (16), it follows that Δ can vanish only if each $\sigma_n = 0$. This, in turn, implies that each $H_{nn} = \omega_n$, the corresponding exact eigenvalue, and that each $\lambda_n = \omega_n$.

Comparing (11) with (3), it follows that, as $\Delta \to 0$, $\tilde{K} \to K$, the true Green's function. Failure of Δ, as defined, to exist indicates that $\tilde{K}$ deviates too greatly from K for the sums over n to converge. Should $\tilde{K}$ depend on one or more adjustable parameters, the minimization condition

$$\delta\Delta = 0, \qquad \delta^2\Delta > 0 \tag{20}$$

would provide an optimization criterion on $\tilde{K}$ analogous to the variational principle for wavefunctions:

Eq. (20) can, in a more abstract sense, be treated as a condition on the functional $\Delta(\tilde{K})$. Applied to (12),

$$\delta\Delta(\tilde{K}) = \operatorname{tr}[\mathscr{S}\delta\tilde{K} \cdot (\mathscr{S}\tilde{K})^*] + \operatorname{tr}[\mathscr{S}\tilde{K} \cdot (\mathscr{S}\delta\tilde{K})^*] = 0 \tag{21}$$

with respect to unrestricted variation in $\tilde{K}$ (consistent however with (i)–(iv) above). Eq. (21) is fulfilled only if $\mathscr{S}\tilde{K}=0$, wherein $\tilde{K}=K$. Eq. (20) thereby represents the variational counterpart of the differential equation $\mathscr{S}K=0$ – being therefore analogous to the Ritz variational theorem for wavefunctions.

It might also be of interest to consider the alternative parameter

$$\Sigma \equiv [\operatorname{tr}\tilde{K}^* \operatorname{tr}\mathscr{S}^2 \tilde{K} - |\operatorname{tr}\mathscr{S}\tilde{K}|^2]_{\tau\mathrm{avg}} \tag{22}$$

which represents the sum of the squares of the energy variances:

$$\Sigma = \sum_n \sigma_n^2 . \tag{23}$$

In place of $\mathscr{S}$ in (22), $\mathscr{H}$ can be written, since dependence on the λ_n cancels out. Clearly, $\Sigma \to 0$ as $\tilde{K} \to K$. Vanishing of Σ is not however a sufficient condition for an exact Green's function: for example, a function having the structure

$$\tilde{K}(q, q', \tau) = \sum_n \psi_n(q)\, \psi_n^*(q')\, e^{-i\lambda_n \tau} \tag{24}$$

in which $\lambda_n \neq \omega_n$ for at least one n, also gives $\Sigma = 0$.

One convenient way to ensure that $\tilde{K}$ has the requisite structure (11) is to employ a known Green's function, say K_0, for a related "unperturbed" Hamiltonian $\mathscr{H}_0$, such that

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{V} . \tag{25}$$

The corresponding Schrödinger operator is then of the form

$$\mathscr{S} = \mathscr{S}_0 - \mathscr{V} , \tag{26}$$

wherein

$$\mathscr{S}_0 K_0 = 0 . \tag{27}$$

Under this simplification, we can write

$$\begin{aligned} \Delta &= \operatorname{tr}[\mathscr{V} K_0 \cdot (\mathscr{V} K_0)^*] \\ \text{and} \quad \Sigma &= [\operatorname{tr} K_0^* \operatorname{tr} \mathscr{V}^2 K_0 - |\operatorname{tr} \mathscr{V} K_0|^2]_{\tau\mathrm{avg}} , \end{aligned} \tag{28}$$

in effect, a transformation to interaction picture.

3. Projecting out the Continuum

Convergence of Δ and Σ might be promoted by eliminating continuum contributions in the corresponding summations. This would be particularly desirable if one were interested only in the discrete spectrum. How to do this is suggested by the asymptotic behavior of continuum eigenfunctions. The limit

$$\lim_{\Delta Q \to \infty} \int_{\Delta Q} |\psi_\nu(q)|^2 \, \mathrm{d}q \tag{29}$$

will not, of course, exist owing to the δ-function normalization of $\psi_\nu(q)$. However for any wavefunction whose asymptotic behavior approaches that of a free particle

$$\int_{\Delta Q} |\psi_\nu(q)|^2 \, \mathrm{d}q = O[(\Delta Q)^N] \tag{30}$$

as $\Delta Q \to \infty$ for some N (not necessarily an integer). This suggests the following definition of the principal part of an improper integral:

$$\mathscr{P} \int F(q)\, \mathrm{d}q \equiv \lim_{\Delta Q \to \infty} \int_{\Delta Q} [F(q) - (\Delta Q)^{N-1} F_N]\, \mathrm{d}q, \tag{31}$$

where

$$F_N \equiv \lim_{\Delta Q \to \infty} \left[(\Delta Q)^{-N} \int_{\Delta Q} F(q)\, \mathrm{d}q\right]. \tag{32}$$

Should (31) itself diverge as $O[(\Delta Q)^{N'}]$ $(N' < N)$, the definition can obviously be generalized to

$$\mathscr{P} \int F(q)\, \mathrm{d}q \equiv \lim_{\Delta Q \to \infty} \int_{\Delta Q} \left[F(q) - \sum_N (\Delta Q)^{N-1} F_N\right] \mathrm{d}q. \tag{33}$$

The latter is likely to pertain to expectation value integrals of the form

$$\int \psi_\nu^*(q) \mathscr{A} \psi_\nu(q)\, \mathrm{d}q. \tag{34}$$

Convergent integrals over normalizable eigenfunctions are retained under the projection operation represented by (31) or (33).

One can generalize further for asymptotic behavior such as $O(e^{\alpha \Delta Q})$ or the like but such instances are unlikely in the present application. The technique will, in fact, fail only if isolated singularities cause $\int_{\Delta Q} F(q)\, \mathrm{d}q$ itself to diverge.

In the case of the free particle itself, the integral (30) goes as $O(V)$ in cartesian coordinates or as $O(V^{1/3}) = O(r)$ in spherical polar coordinates. In either case, the principal part (31) equals zero. Likewise for coulomb wavefunctions, such as hydrogen atom continuum eigenfunctions, the projected overlap integral vanishes.

We assert therefore that application of (33) to a Green's function with the general structure (11) gives

$$\mathscr{P} \operatorname{tr} \mathscr{A} \tilde{K} = \sum_n A_{nn} e^{-i\lambda_n \tau} \tag{35}$$

the original summation having become truncated such as to retain only its discrete components. Of course, the sum (35) might still diverge. But application of this projection technique to calculation of Δ and Σ cannot fail to facilitate convergence. We define accordingly

$$\begin{aligned} \Delta' &\equiv \mathscr{P} \operatorname{tr} [\mathscr{S} \tilde{K} \cdot (\mathscr{S} \tilde{K})^*] = \sum_n [(\lambda_n - H_{nn})^2 + \sigma_n^2] \\ \Sigma' &\equiv [\mathscr{P} \operatorname{tr} \tilde{K}^* \mathscr{P} \operatorname{tr} \mathscr{S}^2 \tilde{K} - |\mathscr{P} \operatorname{tr} \mathscr{S} \tilde{K}|^2]_{\tau \mathrm{avg}} = \sum_n \sigma_n^2. \end{aligned} \tag{36}$$

As $\Delta' \to 0$, the approach of $\tilde{K}$ to K is implied with certainty only with regard to discrete spectral content. But this will be adequate in the applications we propose.

4. Spectral Analysis

Once a Green's function has been optimized in accordance with the foregoing procedures, one can fourier analyze to obtain approximate eigenfunctions and eigenvalues. Specifically, for the discrete eigenvalue spectrum, it is convenient to compute $\operatorname{tr}\tilde{K}$ before spectral analysis. In fact,

$$\mathscr{P}\operatorname{tr}\tilde{K}=\sum_n e^{-i\lambda_n\tau}=\sum_j g_j e^{-i\lambda_j\tau} \tag{37}$$

in which the latter form takes explicit account of degeneracies. Note also that

$$\mathscr{P}\operatorname{tr}\mathscr{H}\tilde{K}=\sum_n H_{nn}e^{-i\lambda_n\tau} \tag{38}$$

and

$$\mathscr{P}\operatorname{tr}\mathscr{H}^2\tilde{K}=\sum_n (H^2)_{nn}e^{-i\lambda_n\tau}\,. \tag{39}$$

By fourier analysis of (38), one can extract both the λ_n as frequencies and the H_{nn} as weight factors. Coupled with analysis of (39), this provides sufficient data to determine the energy variances σ_n(cf. (17)). By Weinstein's theorem [2], some exact eigenvalue must be bracketed by each $H_{nn}\pm\sigma_n$. Stronger bracketing conditions can be deduced by making use of the distribution of neighboring eigenvalues. There does not appear to be any condition relating the λ_n to exact eigenvalues. The best choice of approximate energy eigenvalues is evidently provided by $\tilde{\omega}_n=H_{nn}$, obtained from (38).

The summations (37), (38) and (39) have the form of Dirichlet series for almost periodic functions. It has been assumed in the preceding that they do indeed exist – expecting, at most, a countable set of points τ. This assumption certainly merits further discussion, which we shall defer however until specific cases – e.g. atomic eigenvalue spectra – are taken up.

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Appendix

Structure of $\tilde{K}(q,q',\tau)$

A function obeying condition (i) can be formally expanded in the eigenfunctions of $\mathscr{H}$ as follows:

$$\tilde{K}(q,q',\tau)=\sum_n C_n(q',\tau)\,\psi_n(q)\,. \tag{A.1}$$

By virtue of (ii) however

$$\tilde{K}(q,q',\tau)=\tilde{K}^*(q',q,-\tau)=\sum_n C_n^*(q,-\tau)\,\psi_n^*(q')\,. \tag{A.2}$$

Eqs. (A.1) and (A.2) are therefore consistent with the general bilinear expansion

$$\tilde{K}(q,q',\tau)=\sum_m\sum_n c_{mn}(\tau)\,\psi_n(q)\,\psi_m^*(q') \tag{A.3}$$

with

$$c_{mn}(-\tau)=c_{nm}^*(\tau)\,. \tag{A.4}$$

Property (iii) implies the following composition rule among the coefficients:

$$\sum_k c_{mk}(\tau_1)\,c_{kn}(\tau_2)=c_{mn}(\tau_1+\tau_2)=\sum_k c_{mk}(\tau_2)\,c_{kn}(\tau_1)\,. \tag{A.5}$$

The c-matrices for different τ evidently commute among themselves. They can accordingly be diagonalized by the same unitary transformation. Let $\{\phi_n(q)\}$ represent the basis set arrived at by the corresponding unitary transformation on the eigenfunctions. The expansion (A.3) can therefore be specialized to a quadratic form

$$\tilde{K}(q, q', \tau) = \sum_n c_n(\tau)\, \phi_n(q)\, \phi_n^*(q'), \tag{A.6}$$

whereas (A.5) simplifies to

$$c_n(\tau_1)\, c_n(\tau_2) = c_n(\tau_1 + \tau_2). \tag{A.7}$$

The last relation can only be fulfilled by linear exponential dependence on τ. Consistent with (A.4), in fact,

$$c_n(\tau) = e^{-i\lambda_n \tau}, \tag{A.8}$$

having written $-\lambda_n$ for an arbitrary real constant. Condition (iv) requires lastly that the above summations run over the complete set of basis functions, consistent with the closure relation

$$\sum_n \phi_n(q)\, \phi_n^*(q') = \delta(q - q'). \tag{A.9}$$

We arrive finally at Eq. (11), showing $\tilde{K}$ to have a formal structure analogous to that of K.

The same result can be demonstrated more compactly as follows. Condition (i) implies that there exists some operator $\tilde{\mathscr{T}}(\tau)$ on the same function space as $\mathscr{T}(\tau)$ having the configuration representative

$$\tilde{K}(q, q', \tau) = \langle q' | \tilde{\mathscr{T}}(\tau) | q \rangle \tag{A.10}$$

analogous to (1). If $\tilde{\mathscr{T}}$ is required to be unitary and to obey the composition relation

$$\tilde{\mathscr{T}}(\tau_1)\, \tilde{\mathscr{T}}(\tau_2) = \tilde{\mathscr{T}}(\tau_1 + \tau_2) = \tilde{\mathscr{T}}(\tau_2)\, \tilde{\mathscr{T}}(\tau_1) \tag{A.11}$$

then, by the Stone-von Neumann theorem, it must have the structure

$$\tilde{\mathscr{T}}(\tau) = e^{-i\tau\mathscr{A}}, \tag{A.12}$$

where $\mathscr{A}$ is an hermitian operator on the same space. If λ_n and $\varphi_n(q)$ are, respectively, the eigenvalues and eigenfunctions of $\mathscr{A}$, then $\tilde{\mathscr{T}}(\tau)$ has the spectral representation corresponding to Eq. (11).

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