MINIMIZATION OF THE ENERGY FUNCTIONAL ON A SPECIAL CLASS OF UNITARY OPERATORS

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Conditions of an extremum of the energy functional under transformations of the Hamiltonian corresponding to a change of variables are found. The relationship of these conditions to hypervirial theorems is considered.

When quantum-mechanical problems are solved by methods of approximate separation of variables, like the single-particle approximation and the Born – Oppenheimer approximation, the results depend on the choice of the coordinates system in which the variables are separated [1, 2, 3]. This is as true for problems that are exactly solvable in some coordinate system [3] as for problems that do not admit separation. The best known example is the determination of the ground-state energy of the helium atom by approximate separation of the variables in spherical coordinates and Hylleraas coordinates [4].

In the present paper we pose the problem of finding the coordinate system in which the one-coordinate approximation gives the best energy result. For this we must investigate the extremal conditions of the functional

$$\left\langle \prod_n \varphi_n |\tilde{H}| \prod_n \varphi_n \right\rangle = I(E), \tag{1}$$

where φ_n is the one coordinate function and $\tilde{H}$ ranges over the set of Hamiltonians that describe the given system of particles in all possible coordinates.

We shall assume that the change of φ_n can be formally specified by some change of variables* defined, perhaps, by means of a different functional form for different monotonicity sections of the function φ_n. The corresponding parts of the function must be continued in modulus to the entire domain of definition of the variable, and in the case of a finite domain of definition one may also require continuation of the domain of definition itself. Then the extremum of the functional (1) will not depend on the form of φ_n. Nevertheless, the coordinate transformation itself still depends on φ_n. To avoid this indeterminacy, it is sufficient to assume that the φ_n are solutions of the one-coordinate equations in the original coordinate system.

We shall restrict the treatment to changes of variables that can be described as unitary or isometric transformations of the coordinate operators [5, 6]. In this case the set of operators $\tilde{H}$ in the different coordinate systems will be defined as the set of unitarily transformed operators UHU^+ with unitary operators U of special form corresponding to a change of variables

$$Ux_jU^{-1} = F_j(x_1, \ldots, x_k), \tag{2}$$

$$U = \exp\left[i\sum_{n=1}^{k}\{P_n, f_n(x_1, \ldots, x_k)\}\right], \tag{3}$$

where P_n is the momentum operator conjugate to the coordinate x_n; $f_n(x_1, \ldots, x_k)$ is a function of the coordinates alone; $\{A, B\} = 1/2(AB + BA)$ (the relation between the functions f_n and F_j is briefly considered in the Appendix).

*In the case of a function φ_n that depends on two or more variables this cannot be done.

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Thus, the problem reduces to finding the extremum of the functional $\langle \varphi|UHU^{-1}|\varphi\rangle$, where $\varphi = \prod_n \varphi_n$ is a given function, on the class of unitary operators (3) corresponding to a change of variables.

In order to vary the functions f_n on which the unitary operator depends we use the formulas for differentiating exponential operators with respect to a parameter [7]:

$$\frac{\partial e^{z}}{\partial \lambda} = \int_0^1 dt\, e^{tz} Z'(\lambda) e^{-tz} e^{z} = e^{z}\int_0^1 dt\, e^{-tz} Z'(\lambda) e^{tz}, \tag{4}$$

$$\frac{\partial e^{-z}}{\partial \lambda} = -e^{-z}\int_0^1 dt\, e^{tz} Z'(\lambda) e^{-tz} = -\int_0^1 dt\, e^{-tz} Z'(\lambda) e^{tz} e^{-z}. \tag{5}$$

Using them, we obtain an expression for δU:

$$\delta U = \left[\sum_{s=1}^{k} \frac{\partial}{\partial \alpha_s} \exp\left(i\sum_{j=1}^{k}\{P_j, f_j(x_1,\ldots,x_k)+\alpha_j\}\right)\right]_{\alpha_j=0} = \sum_{s=1}^{k}\int_0^1 dt \exp\left[it\sum_{j=1}^{k}\{P_j, f_j\}\right]\{P_s, \delta f_s\}\exp\left[-it\sum_{j=1}^{k}\{P_j, f_j\}\right] U.$$

Noting that the variations $\delta f_j(x_1, \ldots, x_k)$ are independent, we obtain a system of k equations that must be satisfied for arbitrary δf_j:

$$\begin{gathered}\langle\varphi|[A_s, UHU^{-1}]|\varphi\rangle = 0, \quad s = 1, \ldots, k, \\ A_s = \int_0^1 dt \exp\left[it\sum_{j=1}^{k}\{P_j, f_j\}\right]\{P_s, \delta f_s\}\exp\left[-it\sum_{j=1}^{k}\{P_j, f_j\}\right].\end{gathered} \tag{6}$$

Sufficient conditions for (6) to hold for arbitrary δf_j are (see the Appendix)

$$\int_0^1 dt(\chi_{1s}(\mathbf{x},t)\chi_{4s}^*(\mathbf{x},t) + \chi_{2s}(\mathbf{x},t)\chi_{3s}^*(\mathbf{x},t) + \chi_{3s}(\mathbf{x},t)\chi_{2s}^*(\mathbf{x},t) + \chi_{4s}(\mathbf{x},t)\chi_{1s}^*(\mathbf{x},t)) = 0, \tag{7}$$

where

$$\begin{aligned}\chi_{1s}(\mathbf{x}, t) &= e^{-itz} UHU^{-1}|\varphi\rangle, \\ \chi_{2s}(\mathbf{x}, t) &= e^{-itz}|\varphi\rangle, \\ \chi_{3s}(\mathbf{x}, t) &= P_s e^{-itz} UHU^{-1}|\varphi\rangle, \\ \chi_{4s}(\mathbf{x}, t) &= P_s e^{-itz}|\varphi\rangle,\end{aligned}$$

$$Z = \sum_{j=1}^{k}\{P_j, f_j\}, \qquad s = 1, \ldots, k.$$

The unknown functions f_j here enter the exponent of the exponential operator. This greatly complicates the equations. For the transition to an approximate solution the unknown functions f_j can be represented as expansions in known functions f_{lj} with undetermined coefficients c_{lj}:

$$f_j = \sum_{l=1}^{M} c_{lj} f_{lj}(x_1, \ldots, x_k).$$

If $\{f_{lj}\}$ ($l = 1, 2, \ldots, \infty$) is a complete system of functions, then the equations obtained from the condition of the energy functional,

$$\delta\langle\varphi|U_c H U_c^{-1}|\varphi\rangle = 0,$$

where

$$U_c = \exp\left[i\sum_{j,l}\{P_j, c_{lj} f_{lj}(x_1, \ldots, x_k)\}\right],$$

are equivalent to Eqs. (7). For arbitrary M, the equations have the form

$$\begin{gathered}\langle\varphi|[B_{ls}, U_c H U_c^{-1}]|\varphi\rangle = 0, \quad s = 1, \ldots, k; \ l = 1, \ldots, M, \\ B_{ls} = \int_0^1 dt \exp\left[it\sum_{n,j}\{P_j, c_{nj} f_{nj}\}\right]\{P_s, f_{ls}\}\exp\left[-it\sum_{n,j}\{P_j, c_{nj} f_{nj}\}\right]\end{gathered} \tag{8}$$

or

$$\langle\varphi|U_c[\tilde{B}_{ls}, H]U_c^{-1}|\varphi\rangle = 0, \quad s = 1, \ldots, k; \; l = 1, \ldots, M,$$

$$\tilde{B}_{ls} = \int_0^1 dt \exp\left[-it\sum_{n,j}\{P_j, c_{nj}f_{nj}\}\right]\{P_s, f_{ls}\}\exp\left[it\sum_{n,j}\{P_j, c_{nj}f_{nj}\}\right], \tag{9}$$

depending on which of the relations (4) or (5) are used. The difference between Eqs. (8) and (9) may lie in the different complexity of the calculations. Thus, if the commutator $[\tilde{B}_{ls}, H]$ is simpler than the Hamiltonian itself, it is better to use Eq. (9).

Instead of the unitary operator U_c, we can use a different expression of the unitary operator with the same number of undetermined parameters:

$$U_\pi = U_{11}U_{12}\ldots U_{1M}U_{21}\ldots U_{2M}\ldots U_{kM}, \tag{10}$$

where

$$U_{lj} = \exp[i, \; c_{lj}\{P_l, \; f_{lj}(x_1, \ldots, x_k)\}].$$

The differentiation of U_{lj} with respect to the parameter is simple, as a result of which the derivative of the exponent commutes with the complete unitary operator

$$\frac{\partial}{\partial c_{lj}} U_{lj} = i\{P_l, f_{lj}\}U_{lj} = U_{lj}i\{P_l, f_{lj}\}.$$

Equations for the minimization of the energy functional with the unitary operator given by Eq. (10) have the form

$$\langle\varphi|U_\pi[W_{lj}, \; H]U_\pi^{-1}|\varphi\rangle = 0, \tag{11}$$

where

$$W_{lj} = U_{kM}^{-1}\ldots U_{lj+1}^{-1}\{P_l, \; f_{lj}\}U_{lj+1}\ldots U_{kM}.$$

Equations (11) and (9) are hypervirial relations [5]. Thus, optimization on the class of coordinate systems can be approximately reduced to the requirement that a system of hypervirial relations hold.

APPENDIX

1. We find an explicit expression for the change of variables induced by the given unitary operator.

The direct way consists of summing the commutator series

$$e^A B e^{-A} = B + [A, B] + \frac{1}{2!}[A, [A, B]] + \ldots.$$

However, it is readily summed only for the simplest cases of a change of variables. A much simpler form of the change of variables is obtained when one regards Eq. (2) as a similarity transformation of the Lie algebra that consists of the elements

$$\{P_j f_{1j}(x_1, \ldots, x_k) + f_{2j}(x_1, \ldots, x_k)\}.$$

Then the problem of summing the commutator series can be reduced to the solution of first-order partial differential equations [7]. Introducing in (2) the parameter t:

$$\exp\left\{t\left[\sum_{j=1}^{k}P_j f_j + f_{k+1}\right]\right\}x_j\exp\left\{-t\left[\sum_{j=1}^{k}P_j f_j + f_{k+1}\right]\right\} = \bar{F}(\mathrm{x}, t),$$

and differentiating this equation with respect to t, we arrive at the equation

$$-i\sum_{j=1}^{k} f_j\frac{\partial\bar{F}(\mathrm{x}, t)}{\partial x_j} = \frac{\partial\bar{F}(\mathrm{x}, t)}{\partial t}, \tag{12}$$

which must be solved simultaneously with the initial condition

$$\bar{F}(\mathrm{x}, 0) = x_i. \tag{13}$$

The function $F(\mathbf{x})$ itself can be readily obtained from the solution (12) by setting $t = 1$:

$$F(\mathbf{x}) = \bar{F}(\mathbf{x}, 1).$$

The general solution of Eq. (12) is an arbitrary function of k independent integrals:

$$t + i\int \frac{dx_j}{f_j} = c_j, \quad j = 1, \ldots, k.$$

From the initial condition (13) we determine the actual form of this function:

$$\Phi(g_1, \ldots, g_k) = x_i,$$

where

$$g_j \equiv i\int \frac{dx_j}{f_j}.$$

The determination of the transformed momentum operator

$$\exp\left[\sum_{j=1}^{k} P_j f_j + f_{k+1}\right] P_s \exp\left[-\sum_{j=1}^{k} P_j f_j - f_{k+1}\right] = \sum_{l=1}^{k} P_l F_l + F_{k+1}$$

also reduces to the solution of a system of differential equations:

$$\frac{\partial \bar{F}_l(\mathbf{x}, t)}{\partial t} = \sum_{j=1}^{k}\left[\bar{F}_j(\mathbf{x}, t)\frac{\partial f_l(\mathbf{x})}{\partial x_j} - f_j(\mathbf{x})\frac{\partial \bar{F}_l(\mathbf{x}, t)}{\partial x_j}\right],$$

$$\frac{\partial \bar{F}_{k+1}(\mathbf{x}, t)}{\partial t} = \sum_{j=1}^{k}\left[\bar{F}_j(\mathbf{x}, t)\frac{\partial f_{k+1}(\mathbf{x})}{\partial x_j} - f_j\frac{\partial \bar{F}_{k+1}(\mathbf{x}, t)}{\partial x_j}\right],$$

$$\bar{F}_j(\mathbf{x}, 0) = \delta_{js}, \quad j = 1, \ldots, k, k+1.$$

To within a real additive function, the form of c, the transformed momentum operator, can also be found from the condition that the commutation relations be preserved.

2. In obtaining Eqs. (7) we have used the following assertion: for

$$\langle\varphi_1|H_1\delta A\tilde{H}_1 + H_2\delta A\tilde{H}_2 + \ldots + H_n\delta A\tilde{H}_n + \ldots|\varphi_2\rangle = 0 \tag{14}$$

to hold for arbitrary δA satisfying

$$[\delta A, B] = 0,$$

for given H_1, $\tilde{H}_1$, $H_2, \ldots, \tilde{H}_n, \ldots,$ it is sufficient that

$$\begin{gathered}
\chi_1(B)\chi_1^1(B) + \chi_2(B)\chi_2^1(B) + \ldots + \chi_n(B)\chi_n^1(B) + \ldots = 0, \\
\tilde{H}_1|\varphi_2\rangle = \chi_1^1(B)|\varphi_2\rangle, \quad \langle\varphi_1|H_1 = \langle\varphi_1|\chi_1(B), \\
\cdots\cdots\cdots \\
\tilde{H}_n|\varphi_2\rangle = \chi_n^1(B)|\varphi_2\rangle, \quad \langle\varphi_1|H_n = \langle\varphi_1|\chi_n(B), \\
\cdots\cdots\cdots
\end{gathered} \tag{15}$$

where $\chi_i(B)$ are certain functions of the operator B. This is obviously proved by substituting (15) into (14).

In the text the assertion is used in the case $B \equiv x$, on account of which one can use the multiplicative nature of the operator functions $\chi_i(\mathbf{x})$.

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