Optimisation of parameterised perturbative approximations to wavefunctions

1987 J. Phys. A: Math. Gen. 20 2645

(http://iopscience.iop.org/0305-4470/20/9/045)

J. Phys. A: Math. Gen. **20** (1987) 2645-2647. Printed in the UK

COMMENT

Optimisation of parametrised perturbative approximations to wavefunctions†

S K Kauffmann and S M Perez

Department of Physics, University of Cape Town, Rondebosch 7700, Cape Province, Republic of South Africa

Received 18 August 1986, in final form 7 October 1986

Abstract. Previous work by the authors justified a point-by-point optimisation procedure for parametrised perturbative approximations to wavefunctions by appealing to a principle of minimal sensitivity. Here it is shown that, if the diagonal matrix elements of the perturbation vanish (which can always be arranged via a simple redefinition of the unperturbed Hamiltonian), then the optimisation procedure is also justified by an underlying stationary principle, with the nth-order perturbative approximations being stationary to that order.

In previous work (Kauffmann and Perez 1984, 1986), Stevenson's principle of minimal sensitivity (PMS) (Stevenson 1981) was used to justify the point-by-point optimisation of parametrised perturbative approximations to wavefunctions. As PMS is intuitively, rather than rigorously, based, it is always of interest to seek an independent justification for its use in a given application (Stevenson 1981). It is the purpose of this comment to point out that a certain class of perturbative approximations to wavefunctions is in fact *stationary* with respect to variation of its unperturbed basis set about the exact eigenbasis—indeed the nth-order perturbative approximation turns out to be not only stationary but stationary to the nth order. Thus, for these particular perturbative wavefunction approximations, point-by-point variational optimisation is justified by an underlying stationary principle as well as by PMS.

The perturbative wavefunction approximations in question are entirely determined given any complete orthonormal unperturbed basis set $\{|\phi_k^{(0)}\rangle\}$, which we shall regard as real in order to avoid inessential phase ambiguities. An unperturbed Hamiltonian H_0 is constructed using the diagonal matrix elements of the full Hamiltonian H (Rubinstejn and Yaris 1971),

$$H_0 \equiv \sum_k |\phi_k^{(0)}\rangle\langle\phi_k^{(0)}|H|\phi_k^{(0)}\rangle\langle\phi_k^{(0)}|. \tag{1}$$

The normal Rayleigh-Schrödinger perturbative wavefunction contributions, $|\psi_m^{(1)}\rangle$, $|\psi_m^{(2)}\rangle, \ldots, |\psi_m^{(n)}\rangle, \ldots$, are calculated (Messiah 1963), with the nth-order perturbative approximation $|\psi_m^{(0,1,\ldots,n)}\rangle$ to the exact eigenfunction $|\psi_m\rangle$ of H being the sum of these contributions through order n,

$$|\psi_m^{(0,1,\ldots,n)}\rangle = |\phi_m^{(0)}\rangle + |\psi_m^{(1)}\rangle + \ldots + |\psi_m^{(n)}\rangle \tag{2}$$

† Work supported in part by a CSIR/FRD grant.

0305-4470/87/092645+03$02.50

where $|\psi_m^{(n)}\rangle$ has the expansion

$$|\psi_m^{(n)}\rangle = \sum_k |\phi_k^{(0)}\rangle\langle\phi_k^{(0)}|\psi_m^{(n)}\rangle. \tag{3}$$

The expansion coefficients $\langle\phi_k^{(0)}|\psi_m^{(n)}\rangle$ are messy to write down in the general case, being a sum over expressions whose numerators consist of n-fold products of the matrix elements of the perturbation $V = H - H_0$ and whose denominators consist of n-fold products of differences of diagonal matrix elements of H_0. The essential difference between the present technique, based on the unperturbed H_0 of equation (1), and the usual approach which permits an arbitrary unperturbed H_0, is that the diagonal matrix elements of V vanish here. Hence only off-diagonal matrix elements of V survive in our numerators above and these are in turn equal to the corresponding off-diagonal matrix elements of H itself. Also the diagonal matrix elements of H_0 occurring in our denominators above may be replaced by the corresponding diagonal matrix elements of H itself. Thus the expansion coefficients of equation (3) and hence the perturbative wavefunction approximation $|\psi_m^{(0,1,\ldots,n)}\rangle$ of equation (2) can be expressed *entirely* in terms of the exact Hamiltonian H and the unperturbed basis set $\{|\phi_k^{(0)}\rangle\}$. (This point was apparently not fully appreciated by Rubinstejn and Yaris (1971).)

We now proceed to show that the functional $|\psi_m^{(0,1,\ldots,n)}\rangle$ is stationary to the nth order for variation of $\{|\phi_k^{(0)}\rangle\}$ about $\{|\psi_k\rangle\}$, the exact eigenbasis of H. This variation may be formally expressed in terms of $\{|\delta\phi_k\rangle\}$, where

$$|\phi_k^{(0)}\rangle = |\psi_k\rangle + |\delta\phi_k\rangle \tag{4}$$

and the orthonormality and reality of $\{|\phi_k^{(0)}\rangle\}$ and $\{|\psi_k\rangle\}$ are imposed as restrictions on the variation set $\{|\delta\phi_k\rangle\}$. From the above discussion we have seen that the expansion coefficients $\langle\phi_k^{(0)}|\psi_k^{(n)}\rangle$ of equation (3) consist of sums over n-fold products of off-diagonal matrix elements of H, each divided by an n-fold product of differences of diagonal matrix elements of H. Since the off-diagonal matrix elements of H clearly vanish for the H eigenbasis about which we vary $\{|\phi_k^{(0)}\rangle\}$, we see that $\langle\phi_k^{(0)}|\psi_m^{(n)}\rangle$ and hence $|\psi_m^{(n)}\rangle$ are of order n in the variations $\{|\delta\phi_k\rangle\}$. Now the sum over n of *all* the contributions $|\psi_m^{(n)}\rangle\}$ is the exact result $|\psi_m\rangle$ regardless of the choice of unperturbed basis $\{|\phi_k^{(0)}\rangle\}$, and thus is independent of the variations $\{|\delta\phi_k\rangle\}$. Indeed, we may re-express the $|\psi_m^{(0,1,\ldots,n)}\rangle$ of equation (2) as follows:

$$|\psi_m^{(0,1,\ldots,n)}\rangle = |\psi_m\rangle - \sum_{i=1}^{\infty} |\psi_m^{(n+i)}\rangle. \tag{5}$$

Since $|\psi_m\rangle$ is independent of the variations $\{|\delta\phi_k\rangle\}$ and $|\psi_m^{(n+i)}\rangle$, $i = 1, 2, \ldots$, is of order $(n+i)$ in them, it is clear that $|\psi_m^{(0,1,\ldots,n)}\rangle$ *is stationary to order n in these variations.*

For the case $n = 1$ this theorem was derived using a constructive approach by Biedenharn and Blatt (1954) and Kikuta (1954, 1955). Kikuta also mentioned an iteration method as a means for obtaining a wavefunction approximation which is stationary to a higher order. Biedenharn and Blatt do not consider possible applications, while Kikuta only uses these stationary perturbative wavefunction approximations as sophisticated Rayleigh–Ritz trial functions, useful for optimising approximations to *eigenvalues* of H. The mechanics of how to make use of the stationary property of these wavefunction approximations for direct *wavefunction* (as opposed to eigenvalue) optimisation appear to have eluded these authors. The key to this matter is the realisation that the stationary property of $|\psi_m^{(0,1,\ldots,n)}\rangle$ implies that $\langle x|\psi_m^{(0,1,\ldots,n)}\rangle$ is *separately*

stationary for every value of x (of course, this applies equally well to representations other than the configuration space $\{|x\rangle\}$ one). Thus, if the unperturbed basis set $\{|\phi_k^{(0)}(\lambda)\rangle\}$ depends on a parameter λ, implying that $|\psi_m^{(0,1,\ldots,n)}\rangle$ also depends on λ, we may optimise this parametrised family of perturbative wavefunction approximations directly by requiring that

$$\partial\langle x|\psi_m^{(0,1,\ldots,n)}(\lambda)\rangle/\partial\lambda = 0 \tag{6}$$

at each value of x. In this way λ is obtained as a *function* of x, $\lambda(x)$ and the optimised wavefunction is the object $\langle x|\psi_m^{(0,1,\ldots,n)}(\lambda(x))\rangle$. The above discussion simply parallels that set forth in our previous work (Kauffmann and Perez 1984, 1986), in which PMS rather than an underlying stationary principle was used as the justification for the procedure. Approximations to expectation values of Hermitian operators, in the form $\langle\psi_m^{(0,1,\ldots,n)}(\lambda)|Q|\psi_m^{(0,1,\ldots,n)}(\lambda)\rangle$ (where Q need *not* be H), can also be directly optimised in a manner analogous to that of equation (6). In such cases λ will have no functional dependence.

We note here that in practice the parametrised unperturbed basis $\{|\phi_k^{(0)}(\lambda)\rangle\}$ is to be chosen as close to the exact eigenbasis $\{|\psi_k\rangle\}$ of H as one's skill and understanding of the physics permits. It could, for example, be the known eigenbasis of a solvable parametrised Hamiltonian which well approximates H. The stationarity of the perturbative wavefunctions in $\{|\phi_k^{(0)}\rangle\}$ at $\{|\psi_k\rangle\}$ makes it clear that the better the approximation of $\{|\phi_k^{(0)}\rangle\}$ to $\{|\psi_k\rangle\}$, the better the results can be expected to be. This is completely analogous to the practical criterion for choosing the parametrised trial ground state $|\phi_0^{(0)}(\lambda)\rangle$ in the familiar Rayleigh-Ritz variational method.

Probably the main drawback of this stationary perturbative optimisation approach is that the infinite sums inherent in calculating $|\psi^{(0,1,\ldots,n)}(\lambda)\rangle$ are difficult to carry out, particularly as the perturbative energy denominators are complicated by the special form of H_0 given by equation (1). This complication would seem effectively to rule out certain techniques for carrying out the perturbative sums, such as that of Dalgarno and Lewis (1955). However, in problems where the perturbative sums turn out to be finite or essentially so, as in anharmonic oscillator calculations and perhaps certain quantum field theories, the method could prove to be quite valuable. Work along these lines is currently being undertaken.

References

Biedenharn L C and Blatt J M 1954 *Phys. Rev.* **93** 230
Dalgarno A and Lewis J T 1955 *Proc. R. Soc.* A **233** 70
Kauffmann S K and Perez S M 1984 *J. Phys. A: Math. Gen.* **17** 2027
—— 1986 *J. Phys. A: Math. Gen.* **19** 3807
Kikuta T 1954 *Prog. Theor. Phys.* **12** 10
—— 1955 *Prog. Theor. Phys.* **14** 457
Messiah A 1963 *Quantum Mechanics* (Amsterdam: North-Holland) p 694
Rubinstejn F and Yaris R 1971 *J. Chem. Phys.* **55** 4371
Stevenson P M 1981 *Phys. Rev.* D **23** 2916