TWO NOTES ON PERTURBATION THEORY*

I. INTERCHANGE THEOREMS AND THE VARIATION PRINCIPLE

II. PV IN A DIFFERENT NOTATION

by

Saul T. Epstein

Theoretical Chemistry Institute and Physics Department

University of Wisconsin, Madison, Wisconsin

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I. Interchange Theorems and the Variation Principle

Interchange theorems have been proven and used in Rayleigh Schroedinger perturbation theory[1] and in perturbation theory within the Hartree-Fock approximation.[2] In this note we wish to exhibit the common origin of these theorems and also to indicate that such theorems can be expected to hold in other situations[3], by showing how interchange theorems arise out of the variational principle. We will confine our attention to first order properties.[4]

We consider a Hamiltonian

$$H = H_o + \lambda V + \mu W$$

Let $\tilde{\Psi}$ be an optimal trial function which we have derived from the variational principle:

$$(\delta\tilde{\Psi}, (H-E)\tilde{\Psi}) = 0 \tag{1}$$

$$(\tilde{\Psi}, (H-E)\tilde{\Psi}) = 0 \tag{2}$$

where, for simplicity of notation, we assume everything to be real. We will suppose that, in quite a general way,

$$\tilde{\Psi} = \Psi(\tilde{\varphi}) \tag{3}$$

where $\tilde{\varphi}$ stands for some functions (possibly they are simply constants) which have been determined variationally by free variation of their functional form. We will further assume that $\tilde{\varphi}$ and $\tilde{\Psi}$ can be expanded in a double power series in λ and μ :

$$\tilde{\varphi} = \tilde{\varphi}^{(00)} + \lambda \tilde{\varphi}^{(10)} + \mu \tilde{\varphi}^{(01)} + \lambda\mu \tilde{\varphi}^{(11)} + \cdots$$

$$\tilde{\Psi} = \Psi(\tilde{\varphi}^{(00)}) + \lambda \tilde{\varphi}^{(10)} \left(\frac{\partial \Psi}{\partial \tilde{\varphi}}\right)_{00} + \mu \tilde{\varphi}^{(01)} \left(\frac{\partial \Psi}{\partial \tilde{\varphi}}\right)_{00}$$

$$+ \lambda\mu \left[\tilde{\varphi}^{(11)} \left(\frac{\partial \Psi}{\partial \tilde{\varphi}}\right)_{00} + \tilde{\varphi}^{(10)} \tilde{\varphi}^{(01)} \left(\frac{\partial^2 \Psi}{\partial \tilde{\varphi}^2}\right)_{00} \right] + \cdots \quad (4)$$

$$\equiv \tilde{\Psi}^{(00)} + \lambda \tilde{\Psi}^{(10)} + \mu \tilde{\Psi}^{(01)} + \lambda\mu \tilde{\Psi}^{(11)} + \cdots \quad (5)$$

Inserting these expansions and the corresponding ones for $\delta\tilde{\Psi}$ into (1) and (2) and equating the coefficients of each order to zero we find[5] in particular

$$(\delta \tilde{\Psi}^{(00)}, (H_0 - E^{(00)}) \tilde{\Psi}^{(00)}) = 0 \quad (6)$$

$$
\begin{aligned}
&(\delta\tilde{\Psi}^{(10)}, (H_0 - E^{(00)})\,\tilde{\Psi}^{(01)}) + (\delta\tilde{\Psi}^{(10)}, (W - E^{(01)})\,\tilde{\Psi}^{(00)}) \\
&+ (\tilde{\Psi}^{(10)}, (H_0 - E^{(00)})\,\delta\tilde{\Psi}^{(01)}) + (\delta\tilde{\Psi}^{(01)}, (V - E^{(10)})\,\tilde{\Psi}^{(00)}) \\
&+ (\tilde{\Psi}^{(01)}, (V - E^{(10)})\,\delta\tilde{\Psi}^{(00)}) + (\tilde{\Psi}^{(10)}, (W - E^{(01)})\,\delta\tilde{\Psi}^{(00)}) \\
&+ (\tilde{\Psi}^{(11)}, (H_0 - E^{(00)})\,\delta\tilde{\Psi}^{(00)}) + (\delta\tilde{\Psi}^{(11)}, (H_0 - E^{(00)})\,\tilde{\Psi}^{(00)}) \\
&- E^{(11)}\,(\delta\tilde{\Psi}^{(00)}, \tilde{\Psi}^{(00)}) = 0 \qquad (7)
\end{aligned}
$$

and

$$
\begin{aligned}
\tfrac{1}{2} E^{(11)}\,(\tilde{\Psi}^{(00)}, \tilde{\Psi}^{(00)}) = {} & (\tilde{\Psi}^{(10)}, (H_0 - E^{(00)})\,\tilde{\Psi}^{(01)}) \\
&+ (\tilde{\Psi}^{(11)}, (H_0 - E^{(00)})\,\tilde{\Psi}^{(00)}) + (\tilde{\Psi}^{(10)}, (W - E^{(01)})\,\tilde{\Psi}^{(00)}) \\
&+ (\tilde{\Psi}^{(01)}, (V - E^{(10)})\,\tilde{\Psi}^{(00)}) \qquad (8)
\end{aligned}
$$

Now we have assumed that $\tilde{\varphi}$ is freely variable, hence consider the variation $\delta\tilde{\varphi}^{(10)} = \tilde{\varphi}^{(10)}$ with no other part of $\tilde{\varphi}$ changing. From (4) and (5) this then yields

$$
\delta\tilde{\Psi}^{(10)} = \tilde{\Psi}^{(10)} \quad , \quad \delta\tilde{\Psi}^{(01)} = \delta\tilde{\Psi}^{(00)} = 0
$$

$$
\delta\tilde{\Psi}^{(11)} = \tilde{\varphi}^{(10)}\tilde{\varphi}^{(01)} \left(\frac{\partial^2\Psi}{\partial\tilde{\varphi}^2}\right)_{00} \equiv \Delta
$$

whence from (7) we find

$$(\tilde{\Psi}^{(10)}, (H_0 - E^{(00)})\tilde{\Psi}^{(01)}) + (\tilde{\Psi}^{(10)}, (W - E^{(01)})\tilde{\Psi}^{(00)})$$
$$+ (\Delta, (H_0 - E^{(00)})\tilde{\Psi}^{(00)}) = 0 \qquad (9)$$

Similarly $\delta\tilde{\varphi}^{(01)} = \tilde{\varphi}^{(01)}$ and all other variations zero, yields

$$(\tilde{\Psi}^{(10)}, (H_0 - E^{(00)})\tilde{\Psi}^{(01)}) + (\tilde{\Psi}^{(01)}, (V - E^{(10)})\tilde{\Psi}^{(00)})$$
$$+ (\Delta, (H_0 - E^{(00)})\tilde{\Psi}^{(00)}) = 0 \qquad (10)$$

Finally we note that from (6)

$$(\tilde{\Psi}^{(11)}, (H_0 - E^{(00)})\tilde{\Psi}^{(00)}) = (\Delta, (H_0 - E^{(00)})\tilde{\Psi}^{(00)}) \qquad (11)$$

since $\tilde{\varphi}^{(11)}\left(\frac{\partial\Psi}{\partial\tilde{\varphi}}\right)_{00}$ is in the form of $\delta\tilde{\Psi}^{(00)}$ with $\delta\tilde{\varphi}^{(00)} = \tilde{\varphi}^{(11)}$.

Combining (8) and (11) it then follows from (9) and (10) that we have the interchange theorem

$$\frac{1}{2} E^{(11)}(\tilde{\Psi}^{(00)}, \tilde{\Psi}^{(00)}) = (\tilde{\Psi}^{(10)}, (W - E^{(01)})\tilde{\Psi}^{(00)})$$
$$= (\tilde{\Psi}^{(01)}, (V - E^{(10)})\tilde{\Psi}^{(00)}).$$

Q.E.D.

II. PV in a Different Notation

In this note we wish to derive one of the essential results in the interesting paper of Silverman and van Leuven[3], using a notation which is perhaps more familiar (certainly it is to us). Namely we wish to derive the result which is summarized in the discussion following their equation (24).

We consider now a single perturbation, however we will continue to allow the $\tilde{\varphi}$ to denote a set of functions, not necessarily constants as in reference 3. Then we have instead of (4) and (5)

$$\tilde{\Psi} = \psi(\tilde{\varphi}^{(0)}) + \lambda \tilde{\varphi}^{(1)} \left(\frac{\partial \psi}{\partial \tilde{\varphi}}\right)_0 + \lambda^2 \left[\tilde{\varphi}^{(2)} \left(\frac{\partial \psi}{\partial \tilde{\varphi}}\right)_0 + \frac{1}{2} (\tilde{\varphi}^{(1)})^2 \left(\frac{\partial^2 \psi}{\partial \tilde{\varphi}^2}\right)_0 \right] + \cdots \qquad (12)$$

$$\equiv \tilde{\Psi}^{(0)} + \lambda \tilde{\Psi}^{(1)} + \lambda^2 \tilde{\Psi}^{(2)} + \cdots \qquad (13)$$

while from (1) we derive the sequence of equations

$$(\delta \tilde{\Psi}^{(0)}, (H_0 - E^{(0)}) \tilde{\Psi}^{(0)}) = 0 \qquad (14)$$

$$(\delta\tilde{\Psi}^{(1)}, (H_0 - E^{(0)})\tilde{\Psi}^{(0)}) + (\tilde{\Psi}^{(1)}, (H_0 - E^{(0)})\delta\tilde{\Psi}^{(0)})$$
$$+ \ (\delta\tilde{\Psi}^{(0)}, (V - E^{(1)})\tilde{\Psi}^{(0)}) = 0 \tag{15}$$

$$(\delta\tilde{\Psi}^{(2)}, (H_0 - E^{(0)})\tilde{\Psi}^{(0)}) + (\tilde{\Psi}^{(2)}, (H_0 - E^{(0)})\delta\tilde{\Psi}^{(0)})$$
$$+ (\delta\tilde{\Psi}^{(1)}, (H_0 - E^{(0)})\tilde{\Psi}^{(1)}) + (\delta\tilde{\Psi}^{(1)}, (V - E^{(1)})\tilde{\Psi}^{(0)})$$
$$+ (\tilde{\Psi}^{(1)}, (V - E^{(1)})\delta\tilde{\Psi}^{(0)}) - E^{(2)}(\delta\tilde{\Psi}^{(0)}, \tilde{\Psi}^{(0)}) = 0 \tag{16}$$

$$\vdots$$

etc.

Equation (14) then determines $\tilde{\varphi}^{(0)}$, equation (15) determines $\tilde{\varphi}^{(1)}$, etc. We now remark that in the n'th order equation, $\tilde{\Psi}^{(n)}$, and hence $\tilde{\varphi}^{(n)}$, occurs explicitly in only two terms

$$(\delta\tilde{\Psi}^{(n)}, (H_0 - E^{(0)})\tilde{\Psi}^{(0)}) \tag{17}$$

and

$$(\tilde{\Psi}^{(n)}, (H_0 - E^{(0)})\delta\tilde{\Psi}^{(0)}) \tag{18}$$

Now consider any variation which is such that $\delta\tilde{\varphi}^{(0)}=0$. Then we note the following:

(i) Clearly (18) does not contribute since $\delta\tilde{\psi}^{(0)}=0$.

(ii) The only part of $\delta\tilde{\psi}^{(n)}$ which involves $\tilde{\varphi}^{(n)}$ will be $\delta\tilde{\varphi}^{(n)}\left(\frac{\partial\psi}{\partial\tilde{\varphi}}\right)_0$ which is just in the form of $\delta\tilde{\psi}^{(0)}$ with $\delta\tilde{\varphi}^{(0)}=\delta\tilde{\varphi}^{(n)}$, and hence, from (14) will make no contribution to (17).

Thus we see that variations with $\delta\tilde{\varphi}^{(0)}=0$ lead only to conditions on the <u>lower</u> orderfunctions, conditions which, since these functions have already been determined, must therefore be satisfied automatically in any consistent variational calculation (one can of course also check this explicitly but, as we have said, it must be true if everything is to be consistent). Hence we conclude, in agreement with the result given in reference 3, that only $\tilde{\varphi}^{(0)}$ need be varied in order to determine the $\tilde{\varphi}^{(n)}$.

Footnotes and References

1. A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. A238, 269 (1956); A247, 245 (1958).
2. See M. Cohen and A. Dalgarno, Proc. Roy. Soc. A261, 565 (1961) and many subsequent papers.
3. For example in the PV scheme of J. N. Silverman and J. C. van Leuven, Phys. Rev. 162, 1175 (1967) if extended to double perturbations.
4. For further details on notation, etc. see the review by J. O. Hirschfelder, W. B. Brown and S. T. Epstein in "Advances in Quantum Chemistry" (New York: Academic Press, (1964) Vol. 1, p. 354.
5. See also K. M. Sando and J. O. Hirschfelder, Proc. Nat. Acad. Sci. 52, 434 (1964).