Fermi Energy of Metallic Lithium

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A boundary condition method is developed for deriving the coefficient E_{2n} in the power series expansion of the energy of an electron of wave number k moving in the lattice of an alkali metal. (The entire calculation proceeds within the framework of the Wigner-Seitz atomic sphere approximation.) If the electron wave function is expanded as $\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}(u_0 + u_1 k + u_2 k^2 + \cdots)$ it is shown that the boundary condition $[(\partial/\partial r)(s \text{ part of } u_{2n})]_{r=r_s} = 0$ leads naturally to an evaluation of E_{2n} in terms of values at r_s of homogeneous solutions of the Schrödinger equation and their derivatives with respect to energy and radius. In this way, a simple expression for E_4 is obtained analogous to that derived by Bardeen for E_2. For the case of metallic lithium, this expression leads to the value $E_4 = -0.031$, which agrees with that obtained by the more tedious method of evaluating the expectation value of the Hamiltonian using a wave function correct to the second order in k.

INTRODUCTION

THE author and Kohn[1] have performed a Wigner-Seitz calculation of the coefficient E_4 in the power series expansion for the energy

$$E(k) = E_0 + E_2 k^2 + E_4 k^4 + \cdots, \quad (1)$$

of an electron with wave number k, moving in the lattice of metallic lithium. The method consists in a straightforward evaluation[2] of the expectation value of the appropriate Hamiltonian using a wave function correct to the second order in k. The value of the cohesive energy obtained by a linear variation function method[1] was combined with several small corrections by Herring,[3] who obtained a theoretical value for the cohesive energy of lithium which agrees with the experimental value to within the probable error in either.

Although the linear variation function method gives more accurate results than those obtained from the power series (1), we present here a boundary condition method of obtaining the general coefficient E_{2n}, which avoids evaluating an expectation value of the Hamiltonian. In particular, we shall arrive quite directly at the expression for E_2 derived by Bardeen.[4]

BARDEEN'S PROCEDURE

If we write the wave function of an electron in the lattice of metallic lithium[5] as a power series in k

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[1] R. A. Silverman and W. Kohn, Phys. Rev. 80, 912 (1950).

[2] A numerical error was subsequently discovered which modifies the value of the entries of Table I of reference 1 to those given in an erratum, Phys. Rev. 82, 283 (1951).

[3] C. Herring, Phys. Rev. 82, 282 (1951).

[4] J. Bardeen, J. Chem. Phys. 6, 367 (1938). Bardeen was concerned only with the construction of u_1, but his procedure is applicable to the construction of the general u_n, as we shall see below.

[5] The following considerations apply to any monovalent metal to the extent that there is available a radial ion-core potential which takes into account adequately the interaction between the closed-shell and valence electrons. This is certainly the case for lithium and sodium. See discussion in F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 348.

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}(u_0 + u_1 k + u_2 k^2 + \cdots), \quad (2)$$

(neglecting any dependence on the direction of $\mathbf{k}$, which is, of course, a fundamental weakness of this approach), the Schrödinger equation[6]

$$(-\nabla^2 + V(r))\psi_k(\mathbf{r}) = E(k)\psi_k(\mathbf{r}), \quad (3)$$

separates into the following set of equations familiar from ordinary perturbation theory:

$$(-\nabla^2 + V - E_0)u_0 = 0,$$
$$(-\nabla^2 + V - E_0)u_1 = 2i(\partial u_0/\partial z),$$
$$(-\nabla^2 + V - E_0)u_2 = 2i(\partial u_1/\partial z) + (E_2 - 1)u_0,$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$
$$(-\nabla^2 + V - E_0)u_{2n} = 2i(\partial u_{2n-1}/\partial z) + (E_2 - 1)u_{2n-2} \quad (4)$$
$$+ \cdots + E_{2n}u_0,$$
$$(-\nabla^2 + V - E_0)u_{2n+1} = 2i(\partial u_{2n}/\partial z) + (E_2 - 1)u_{2n-1}$$
$$+ \cdots + E_{2n}u_1,$$
$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

Here we have chosen $\mathbf{k}$ along the z axis of a spherical coordinate system. $V(r)$ is the empirical ion-core potential computed by Seitz.[7]

The procedure adopted by Bardeen[4] is to find particular solutions of the set (4) by inspection. These are then made to satisfy the Wigner-Seitz boundary condition[8] by adding appropriate multiples of solutions of the homogeneous equation

$$(-\nabla^2 + V - E_0)\psi = 0. \quad (5)$$

Consider, for example, the second equation of (4),

[6] Length is measured in units of the Bohr radius, energy in Rydberg units.

[7] F. Seitz, Phys. Rev. 47, 400 (1935). Although Seitz used the correct ion-core potential in deriving the results reported in this reference, Herring discovered a small but significant error in the published potential. Bardeen kindly supplied us with the correct potential.

[8] It will be recalled that if f is even, the Wigner-Seitz boundary condition is $\partial f(r_s)/\partial r = 0$, where r_s is the radius of the s-sphere, whereas if f is odd, the boundary condition is $f(r_s) = 0$. The ground-state wave function u_0 is even, so that by the construction given below, u_i is even if i is even, odd if i is odd. The value E_0 occurring in (5) is determined by the boundary condition $\partial u_0(r_s)/\partial r = 0$.

namely

$$(-\nabla^2+V-E_0)u_1 = 2i(\partial u_0/\partial z). \qquad (6)$$

By inspection, $-izu_0$ is a particular solution of (6). The complete solution must satisfy the boundary condition $u_1(r_s)=0$; this can be achieved by adding an appropriate multiple of the p solution of (5). Thus, the desired solution of (6) is

$$u_1 = iz(f_p/r - u_0), \qquad (7)$$

where f_p is the radial part of the p solution of (5) which satisfies $f_p(r_s) = r_s u_0(r_s)$.

Now we place (7) in the expectation value[9]

$$\frac{\int_V (u_0+u_1 k)^*(-\nabla^2+V-2ik\partial/\partial z+k^2)u_0 d\tau}{\int_V (u_0+u_1 k)^* u_0 d\tau}, \qquad (8)$$

which represents $E(k)$ correct to second order in k. (V=volume of the s-sphere.) By some ingenious manipulation, Bardeen was able to transform the resultant expression for E_2 into

$$E_2 = \gamma(r f_p'/f_p)_{r=r_s}, \qquad (9)$$

where $f_p' = \partial f_p/\partial r$[10] and $\gamma = (4\pi/3)r_s^3 u_0^2(r_s)$; u_0 is normalized, i.e.,

$$\int_V u_0^2 d\tau = 1.$$

We have discovered that the boundary condition

$$\left[\frac{\partial}{\partial r}(s \text{ part of } u_{2n})\right]_{r=r_s}$$

will lead automatically to the expression (9) for E_2, and to similar, more complicated expressions for E_4, E_6, etc. Let us first evaluate E_2 by this method.

EVALUATION OF E_2 BY BOUNDARY CONDITION METHOD

Consider the third equation of the set (4), namely

$$(-\nabla^2+V-E_0)u_2 = 2i\partial u_1/\partial z + (E_2-1)u_0. \qquad (10)$$

If we operate on $-izu_1+\frac{1}{2}z^2u_0$ with $(-\nabla^2+V-E_0)$, we obtain $2i\partial u_1/\partial z - u_0$, which differs from the right-hand side of (10) only by the absence of the factor E_2u_0. Thus if f has the property that

$$(-\nabla^2+V-E_0)f = u_0, \qquad (11)$$

a particular solution of (10) is $-izu_1+\frac{1}{2}z^2u_0+E_2f$. Such an f is given formally by differentiating $(-\nabla^2+V-E)u_0(E,r)=0$ with respect to E, and then setting $E=E_0$.[11] This gives

$$(-\nabla^2+V-E_0)(\partial u_0/\partial E)_{E=E_0} = u_0. \qquad (12)$$

Thus,

$$-izu_1+\frac{1}{2}z^2u_0+E_2(\partial u_0/\partial E)_{E=E_0} \qquad (13)$$

is a particular solution of (10). Recalling (7), it is seen that (13) is a linear combination of s and d functions. Therefore, the radial derivatives of the s and d parts of (13) must vanish at the surface of the s-sphere. To insure this we add appropriate multiples of s and d solutions of the homogeneous Eq. (4). Accordingly, the complete solution is

$$u_2 = (\tfrac{2}{3}rf_p - \tfrac{1}{3}r^2u_0 + c_d f_d)P_2 + (\tfrac{1}{3}rf_p - \tfrac{1}{6}r^2u_0 \\ + E_2(\partial u_0/\partial E)_{E=E_0} + c_s u_0)P_0. \qquad (14)$$

Here P_0, P_2 are Legendre polynomials, and c_s, c_d are constants; f_d satisfies

$$\left(-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+V+\frac{6}{r^2}-E_0\right)f_d = 0. \qquad (15)$$

(Henceforth when $E=E_0$ and $r=r_s$ appear as subscripts, they will be abbreviated as E_0 and r_s, respectively.)

As far as the definition of $u_0(E,r)$ for values of E not equal to E_0 is concerned, we observe that $(\partial u_0(E,r)/\partial E)_{E_0}$ satisfies (10) provided the function $u_0(E,r)$ reduces continuously to $u_0(E_0,r)$ when E approaches E_0. Thus, if we define $u_0^n(E,r)$ as the solution of $(-\nabla^2+V-E)u_0^n(E,r)=0$ which is normalized for any E, $u_0(E,r)$ is given by $F(E)u_0^n(E,r)$, where $F(E)$ is any continuous function of E such that $F(E_0)=1$. Then we have

$$(\partial u_0(E,r)/\partial E)_{E_0} = F'(E_0)u_0^n(E_0,r) \\ + (\partial u_0^n(E,r)/\partial E)_{E_0}, \qquad (16)$$

i.e., any two definitions of $u_0(E,r)$ lead to values of $(\partial u_0(E,r)/\partial E)_{E_0}$ which differ only by a multiple of $u_0(E_0,r)$, a difference which is already within the arbitrariness of the functions u_n. [This fact is apparent from the form of (4).] Moreover, since $u_0'(E_0,r_s)=0$, it is clear that $(\partial^2 u_0/\partial r\partial E)_{r_s,E_0}$ is uniquely defined.

Now we set the s part of (14) equal to zero:

$$\tfrac{1}{3}r_s f_p'(r_s) + E_2(\partial^2 u_0/\partial r\partial E)_{r_s,E_0} = 0, \qquad (17)$$

i.e.,

$$E_2 = -\tfrac{1}{3}r_s f_p'(r_s)/(\partial^2 u_0/\partial r\partial E)_{r_s,E_0}. \qquad (18)$$

The quantity $(\partial^2 u_0/\partial r\partial E)_{r_s,E_0}$ can be evaluated by multiplying both sides of (12) by u_0, integrating over

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[9] If $\psi^{(m)}$ and $\psi^{(n)}$ represent the true wave function to orders m and n, respectively, $\int \psi^{(m)*}H\psi^{(n)}d\tau/\int \psi^{(m)*}\psi^{(n)}d\tau$ represents the energy correct to order $m+n+1$.

[10] "Prime" will have this meaning hereafter.

[11] This procedure was originated by C. Herring and A. G. Hill in their paper on metallic beryllium, Phys. Rev. **58**, 132 (1940). These authors constructed an expression equivalent to Eq. (14).

the s-sphere, and invoking Green's theorem.[12] Thus,

$$\int_V u_0(-\nabla^2+V-E_0)(\partial u_0/\partial E)_{E_0}d\tau = \int_V u_0^2 d\tau = 1,$$

$$\int_V (\partial u_0/\partial E)_{E_0}(-\nabla^2+V-E_0)u_0 d\tau$$

$$+\int_s \{-u_0(\partial^2 u_0/\partial r\partial E)_{r_s,E_0} \qquad (19)$$

$$+(\partial u_0/\partial r)(\partial u_0/\partial E)_{E_0}\}d\sigma = 1,$$

$$-4\pi r_s^2 u_0(r_s)(\partial^2 u_0/\partial r\partial E)_{r_s,E_0} = 1,$$

$$(\partial^2 u_0/\partial r\partial E)_{r_s,E_0} = -1/4\pi r_s^2 u_0(r_s).$$

Substituting this value into (17), we find

$$E_2 = (4\pi/3)r_s^3 u_0^2(r_s)(rf_p'/f_p)_{r_s}, \qquad (20)$$

using $f_p(r_s) = r_s u_0(r_s)$. This is precisely the expression obtained by Bardeen as described above.

CONSTRUCTION OF u_n

We have seen that u_n must satisfy

$$(-\nabla^2+V-E_0)u_n = 2i\partial u_{n-1}/\partial z+(E_2-1)u_{n-2}$$
$$+\cdots+E_n u_0 \quad (n \text{ even}),$$
$$(-\nabla^2+V-E_0)u_n = 2i\partial u_{n-1}/\partial z+(E_2-1)u_{n-2}$$
$$+\cdots+E_n u_1 \quad (n \text{ odd}). \qquad (21)$$

If we assume that u_n starts as

$$-\left[\frac{(iz)^n}{n!}u_0+\frac{(iz)^{n-1}}{(n-1)!}u_1+\cdots+izu_{n-1}\right], \qquad (22)$$

it can easily be shown that the difference between the right-hand side of (21) and the result of operating on (22) with $(-\nabla^2+V-E_0)$ consists only of terms involving solutions of the homogeneous Schrödinger equation (5) and their E derivatives of various orders evaluated at E_0. These terms can be generated by operating with $(-\nabla^2+V-E_0)$ on higher E derivatives of said homogeneous solutions.[13] Finally, suitable multiples of the homogeneous solutions themselves must be added to the sum of (22) and these E derivatives in order to satisfy the appropriate boundary condition at the surface of the s-sphere. For example, if we apply $(-\nabla^2+V-E_0)$ to (22) for the case $n=3$, we find that the difference between the resulting expression and the right-hand side of the third equation of (4) is $iE_2 P_1 f_p$; similarly, for $n=4$ the difference is $E_4 u_0+E_2 c_d P_2 f_d +E_2^2(\partial u_0^n/\partial E)_{E_0}$. Accordingly, the complete solutions

[12] This use of Green's theorem was suggested by W. Kohn.
[13] Note that in differentiating $(-\nabla^2+V-E)u_0^n=0$ more than once with respect to E, it is vital that the wave function be the normalized function u_0^n.

u_3 and u_4 are given by

$$u_3 = \tfrac{1}{6}iz^3 u_0+\tfrac{1}{2}z^2 u_1-izu_2+iE_2 P_1(\partial f_p/\partial E)_{E_0}$$
$$+c_p P_1 f_p+c_f P_3 f_f$$

$$u_4 = -(1/24)z^4 u_0+\tfrac{1}{6}iz^3 u_1+\tfrac{1}{2}z^2 u_0-izu_3 \qquad (23)$$
$$+E_4(\partial u_0/\partial E)_{E_0}+\tfrac{1}{2}E_2^2(\partial^2 u_0^n/\partial E^2)_{E_0}$$
$$+E_2 c_d P_2(\partial f_d/\partial E)_{E_0}+\gamma_s u_0+\gamma_d P_2 f_d+\gamma_g P_4 f_g,$$

where the c's and γ's are constants, P_l is the Legendre polynomial of degree l, and f_l is the radial solution of (6) with angular momentum quantum number l.

It will be observed that u_{2n} must contain the term E_{2n} in order to generate the $E_{2n}u_0$ term appearing in the right-hand side of (21). This accounts for the possibility of evaluating E_{2n} from the boundary condition

$$\left[\frac{\partial}{\partial r}(s \text{ part of } u_{2n})\right]_{r_s}=0. \qquad (24)$$

For, since $u_0'(r_s)=0$, the equation obtained from (24) cannot be satisfied by appropriate choice of a multiple of u_0 added to u_{2n}. Inasmuch as $(\partial^2 u_0/\partial r\partial E)_{r_s,E_0}\neq 0$, the boundary condition (24) represents an equation which can be solved explicitly for E_{2n}.

EVALUATION OF E_4

We now give an outline of the algebra leading from the expression (23) for u_4 to a simple formula for E_4, via the boundary condition $[(\partial/\partial r)(s \text{ part of } u_4)]_{r_s}=0$. The algebra is straightforward but somewhat tedious; we will outline only the principal steps.

The radial derivative of the s part of u_4 evaluated at $r=r_s$ turns out to be

$$\frac{1}{30}r_s^3 u_0(r_s)-\frac{1}{10}r_s^2 f_p(r_s)-\frac{1}{30}r_s^3 f_p'(r_s)$$

$$-\frac{1}{3}r_s E_2\left(\frac{\partial u_0}{\partial E}\right)_{r_s,E_0}-\frac{1}{6}r_s^2 E_2\left(\frac{\partial^2 u_0}{\partial r\partial E}\right)_{r_s,E_0}$$

$$-\frac{2}{15}r_s c_d f_d(r_s)-\frac{1}{15}r_s^2 c_d f_d'(r_s)+\frac{1}{3}E_2\left(\frac{\partial f_p}{\partial E}\right)_{r_s,E_0}$$

$$+\frac{1}{3}E_2 r_s\left(\frac{\partial^2 f_p}{\partial r\partial E}\right)_{r_s,E_0}-\frac{i}{3}c_p f_p(r_s)-\frac{i}{3}r_s c_p f_p'(r_s)$$

$$+\frac{1}{2}E_2^2\left(\frac{\partial^3 u_0^n}{\partial r\partial E^2}\right)_{r_s,E_0}+E_4\left(\frac{\partial^2 u_0}{\partial r\partial E}\right)_{r_s,E_0}. \qquad (25)$$

We are able to choose the following particularly convenient definition for $f_p(E, r_s)$ at points other than E_0:

$$f_p(E, r_s) = r_s u_0^n(E, r_s). \qquad (26)$$

It can easily be shown that the additional terms created by any other definition are canceled by the accompanying change in c_p. Thus we have

$$(\partial f_p/\partial E)_{r_s,E_0} = r_s(\partial u_0/\partial E)_{r_s,E_0}, \qquad (27)$$

as well as $f_p(r_s) = r_s u_0(r_s)$. To reduce (25) further, we must evaluate c_p, which is determined by the boundary condition (p part of u_3)$_{r_s} = 0$. The p part of u_3 can be found by reductions exactly analogous to those made in finding the s part of u_4. The result is

$$(\text{p part of } u_3) = \frac{1}{10}ir^3 u_0 - \frac{3}{10}ir^2 f_p - irE_2\left(\frac{\partial u_0}{\partial E}\right)_{E_0}$$

$$-\frac{2}{5}irc_d f_d + iE_2\left(\frac{\partial f_p}{\partial E}\right)_{E_0} + c_p f_p, \quad (28)$$

which leads immediately to the following expression for c_p:

$$c_p = [ir_s/5 f_p(r_s)][r_s^2 u_0(r_s) + 2c_d f_d(r_s)]. \quad (29)$$

The value of c_d is obtained from

$$c_d f_d'(r_s) = 2E_2(\partial^2 u_0/\partial r \partial E)_{r_s, E_0}, \quad (30)$$

which is an immediate consequence of comparing the radial derivatives of the s and d parts of u_2 [see Eq. (14)]. We have now reduced (25) to

$$\frac{1}{30}r_s^3 u_0(r_s)\left(\frac{r f_p'}{f_p}\right)_{r_s} - \frac{1}{6}E_2 r_s^2\left(\frac{\partial^2 u_0}{\partial r \partial E}\right)_{r_s, E_0}$$

$$+\frac{1}{3}E_2 r_s\left(\frac{\partial^2 f_p}{\partial r \partial E}\right)_{r_s, E_0} + E_4\left(\frac{\partial^2 u_0}{\partial r \partial E}\right)_{r_s, E_0}$$

$$+\frac{1}{2}E_2^2\left(\frac{\partial^3 u_0^n}{\partial r \partial E^2}\right)_{r_s, E_0} + \frac{2}{15}E_2 r_s^2\left(\frac{\partial^2 u_0}{\partial r \partial E}\right)_{r_s, E_0}$$

$$\times\left[2\left(\frac{r f_p'}{f_p}\right)_{r_s}\left(\frac{r f_d'}{f_d}\right)_{r_s}^{-1} - 1\right]. \quad (31)$$

The quantity $(\partial^3 u_0/\partial r \partial E^2)_{r_s, E_0}$ can be evaluated in a fashion similar to that used to evaluate $(\partial^2 u_0/\partial r \partial E)_{r_s, E_0}$. Multiply both sides of

$$\tfrac{1}{2}(-\nabla^2 + V - E_0)(\partial^2 u_0^n/\partial E^2)_{E_0} = (\partial u_0^n/\partial E)_{E_0}, \quad (32)$$

by u_0^n and integrate over the volume of the s-sphere, using Green's theorem. Then

$$\frac{1}{2}\int_V u_0^n(-\nabla^2 + V - E_0)\left(\frac{\partial^2 u_0^n}{\partial E^2}\right)_{E_0} d\tau$$

$$= \int_V u_0^n\left(\frac{\partial u_0^n}{\partial E}\right)_{E_0} d\tau = \frac{1}{2}\frac{d}{dE}\int_V u_0^{n2} d\tau = 0, \quad (33)$$

or finally

$$(\partial^3 u_0^n/\partial r \partial E^2)_{r_s, E_0} = 0. \quad (34)$$

The evaluation of $(\partial^2 f_p/\partial r \partial E)_{r_s, E_0}$ requires a little more care, but is otherwise quite straightforward. The analysis is as follows: if Φ_p denotes the numerical solution of the equation

$$\left(-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + V + \frac{2}{r^2} - E_0\right)\Phi_p = 0. \quad (35)$$

Equation (26) requires that

$$f_p(r, E) = \frac{r_s u_0(r_s, E)}{\Phi_p(r_s, E)}\Phi_p(r, E). \quad (36)$$

Introducing $P = r\Phi_p$, we obtain after some manipulation

$$\left(\frac{\partial^2 f_p}{\partial r \partial E}\right)_{r_s, E_0} = \gamma^{-1}E_2\left(\frac{\partial u_0^n}{\partial E}\right)_{r_s, E_0}$$

$$+r_s u_0(r_s, E_0)\frac{d}{dE}\left(\frac{P'(r_s, E)}{P(r_s, E)}\right)_{E_0}. \quad (37)$$

We have cast $(\partial^2 f_p/\partial r \partial E)_{r_s, E_0}$ into this form because it is especially easy to evaluate numerically in terms of functions we have already tabulated in connection with our previous work.[1] $\Big($Note that $\{(d/dE)[P'(r_s, E)/P(r_s, E)]\}_{E_0}$ is easily converted into the simpler form

$$-\int_0^{r_s} P^2(E_0, r)dr/P^2(E_0, r_s).\Big)$$

Setting (31) equal to zero, we finally find

$$\frac{E_2}{40\pi u_0(r_s)} + \frac{E_2}{24\pi u_0(r_s)} + \frac{1}{3}E_2 r_s(\partial^2 f_p/\partial r \partial E)_{r_s, E_0}$$

$$\frac{E_4}{4\pi r_s^2 u_0(r_s)} - \frac{E_2^2}{15\pi\gamma u_0(r_s)}(r f_d'/f_d)_{r_s}^{-1}$$

$$+\frac{E_2}{30\pi u_0(r_s)} = 0, \quad (38)$$

or, combining terms and solving for E_4:

$$E_4 = (2/5)r_s^2 E_2 - (4/15)E_2^2\gamma^{-1}r_s^2(r f_d'/f_d)_{r_s}^{-1}$$

$$+\gamma E_2(\partial^2 f_p/\partial r \partial E)_{r_s, E_0}/u_0(r_s). \quad (39)$$

Substituting the appropriate numerical values into (39), we obtain $E_4 = -0.031$, which represents a cohesive energy correction of $+0.5$ kcal/M. The discrepancy between the value of E_4 obtained by this method and that obtained by the expectation value method (-0.029) amounts to about 0.03 kcal/M, which is much less than experimental accuracy. Inasmuch as both methods yield E_4 as a difference of large numbers, with consequent loss of one significant figure, this discrepancy is easily accounted for despite the fact that our wave functions are known to be accurate to within less than one percent.

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