SOME ASPECTS OF CHEMISORPTION: THE INDIRECT INTERACTION AND THE SHORT-CHAIN MODEL

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Appendix

ASYMPTOTIC FORM OF THE PAIR INTERACTION

The evaluation of the asymptotic behavior of G_{12}^{X} is laborious and complicated. Only in the <10> and <11> directions is the calculation reasonably direct. We shall find that the pair interaction decays according to an R^{-5} inverse power law. It is proportional to an anisotropic oscillatory factor in E_F. The envelope function for the Green's function for fixed R has critical points at $E_c = \pm 3, \pm 1$; these are $|E - E_c|^{1/2}$ at the band edges, and $|E - E_c|^{1/2}$ or $|E - E_c|^{-1/2}$ at $E_c = \pm 1$ in the <10> or <11> direction, respectively.

In order to evaluate the asymptotic form of the pair interaction, we must find the asymptotic form of the pair Green's function, $G_{12}^{X}(E)$. Naturally, this function becomes arbitrarily small. It is thus permissable to expand eqn. (3.25) to

$$\Delta W_{pair} \sim \frac{2}{\pi} \operatorname{Im} \int_{-\infty}^{E_F} V^4 \, \bar{G}_{aa}^{X\,2}(E) \, G_{12}^{X\,2}(E) \, dE \tag{A.1}$$

We recall eqns. (3.3), (3.1), (3.6), (3.2)

$$G_{ij}^{A}(E) = \sum_{|k_x|,|k_y| \le \pi} G_{11}(E, k_{\parallel}) \, e^{i(k_x m + k_y n)},$$

$$G_{11}(E, k_{\parallel}) = 2\left(\omega + i\sqrt{1-\omega^2}\right),$$

$$\omega = E + \cos k_x + \cos k_y$$

where we have taken T = 1/2, as in our calculations, m = i - 1,

$n = j - 1$, and redefined $k_x a$ as k_x and similarly for k^y (or set $a = 1$). The two cases <10> and <11> correspond to $n = 0$ and $n = m$, respectively.

We transform the summation to an integral:

$$G_{ij}^{A}(E) = \frac{2}{(2\pi)^2}\int_{-\pi}^{\pi} dk_x \int_{-\pi}^{\pi} dk_y \, (\omega + i\sqrt{1-\omega^2})\, e^{ik_x m} e^{ik_y n} \tag{A.2}$$

Since the integrand is identical on opposite points of the domain, we cannot do an endpoint expansion. The asymptotic behavior arises from singularities in the interior. Moreover, since the exponent is flat, we cannot use a stationary phase approach. We must resort to the method of generalized functions, as treated by Lighthill.(L3) The asymptotic behavior will spring from the points where the Fourier-transformed function is not smooth. In this case, ω is smooth, but $\sqrt{1 - \omega^2}$ is not infinitely differentiable where ω is ± 1. Hence we can drop ω from subsequent treatment.

To find the <10> behavior, we will consider the form of

$$G_x \equiv \int_{-\pi}^{\pi} e^{ikm}\, i\sqrt{1-\omega^2}\, dk \tag{A.3}$$

for large integers m. The phase of the square root is such that

$$i\sqrt{1-\omega^2} = |\omega^2 - 1|^{1/2} \times \begin{cases} i & |\omega| < 1 \\ -\operatorname{sgn}(\omega) & |\omega| > 1 \end{cases} \tag{A.4}$$

Let us define

$$\mathcal{E} \equiv E + \cos k_y \Rightarrow \omega = \mathcal{E} + \cos k_x \quad \text{(A.5)}$$

We see that there will be singularities in the integrand at $\omega = 1$. First we focus on the singularity at $\gamma = 1$. Only for $0 < \mathcal{E} < 2$ can $\omega = 1$. Suppose we define k_+ such that $k_+ > 0$ and $\cos k_+ = 1 - \mathcal{E}$. Then for $K \equiv k - k_+$ small

$$\begin{aligned} |\omega^2 - 1|^{1/2} &= \left|\left[\mathcal{E} + \cos(K + k_+)\right]^2 - 1\right|^{1/2} \\ &= \left|(1 - \sin K \sin k_+)^2 - 1\right|^{1/2} \\ &\approx \left|2K\sqrt{1-(1-\mathcal{E})^2}\right|^{1/2} \end{aligned} \quad \text{(A.6)}$$

An identical expansion holds about $-k_+$. The fundamental integral we will use is (L3)

$$I_+(0) \equiv \int e^{ikm} |k|^{1/2} \theta(k) dk = \frac{\sqrt{\pi}}{2} e^{\frac{3\pi i}{4}} m^{-3/2} \quad \text{(A.7)}$$

where θ is the unit step function (Heaviside function). It follows that

$$\begin{aligned} I_+(k_0) &\equiv \int e^{ikm} |k - k_0|^{1/2} \theta(k - k_0) dk \\ &= e^{ik_0 m} I_+(0) = \frac{\sqrt{\pi}}{2} e^{3\pi i/4} e^{ik_0 m} m^{-3/2} \end{aligned} \quad \text{(A.8)}$$

$$\begin{aligned} I_-(k_0) &\equiv \int e^{ikm} |k - k_0|^{1/2} \theta(-(k - k_0)) dk = e^{ik_0 m} I_-(0) \\ &= e^{ik_0 m} I_+(0)^* = \frac{\sqrt{\pi}}{2} e^{-3\pi i/4} e^{ik_0 m} m^{-3/2} \end{aligned} \quad \text{(A.9)}$$

We thus find the contribution from $\omega = +1$ to be (for 0

$0 < \varepsilon < 2$)

$$G_x = \left\{ e^{ik_+ m}\left[i I_+(0) - I_-(0)\right] + e^{-ik_+ m}\left[-I_+(0) + i I_-(0)\right]\right\} \sqrt{2}\,(1-(1-\varepsilon)^2)^{1/4}$$

$$= \sqrt{\tfrac{\pi}{2}}\,(1-(1-\varepsilon)^2)^{1/4}\, m^{-3/2}\Big[\left(e^{5\pi i/4} - e^{-3\pi i/4}\right) e^{ik_+ m} + \left(e^{-3\pi i/4} + e^{-i\pi/4}\right) e^{-ik_+ m}\Big]$$

$$= \sqrt{2\pi}\,(1-(1-\varepsilon)^2)^{1/4}\, m^{-3/2}\, e^{-i\pi/4}\, e^{-ik_+ m} \tag{A.10}$$

For $-2 < \varepsilon < 0$, the $\omega = -1$ singularity contributes similarly. We define $k_- > 0$ by $\cos k_- = -1 - \varepsilon$, let $K = k - k_-$, and find

$$|\omega^2 - 1|^{1/2} \approx \left| 2K\sqrt{1-(1+\varepsilon)^2}\right|^{1/2} \tag{A.11}$$

The contribution from $\omega = -1$ is

$$G_x = \left\{ e^{ik_- m}\left[+ I_+(0) + i I_-(0)\right] + e^{-ik_- m}\left[+i I_+(0) + I_-(0)\right]\right\} \times \sqrt{2}\,\left(1-(1+\varepsilon)^2\right)^{1/4}$$

$$= -\sqrt{2\pi}\,\left(1-(1+\varepsilon)^2\right)^{1/4} m^{-3/2}\, e^{i\pi/4}\, e^{-ik_- m} \tag{A.12}$$

We are now left with

$$G_{m+1,1}(\varepsilon) = \frac{2}{(2\pi)^2}\int_{-\pi}^{\pi} dk_y\, G_x(k_y) \tag{A.13}$$

This time we are fortunate to see that G_x contains an exponential which is not flat, so that we can use the method of stationary phase,[C3,E3] which we write in a form convenient for application here. Suppose

$$f(m) = \int_a^b e^{-imh(k)} g(k)\, dk$$

where h(k) and g(k) are real and (a,b) is on the real axis. Let there be one point $k_o \epsilon (a,b)$ such that $h'(k_o) = 0$ but $h''(k_o) \neq 0$. Then

$$f(m) \sim \left[\frac{2\pi}{m|h''(k_o)|}\right]^{1/2} g(k_o) \exp\left[-imh(k_o) \mp \frac{i\pi}{4} \operatorname{sgn}(h''(k_o))\right] \tag{A.14}$$

From (A.5) we see that we must distinguish several regions of energy E. Since $|\varepsilon| < 2$, for $|E|>3$ we pick up no contribution. This is what we would expect for the imaginary part of G_{ij}, as we are outside the band. The absence of a real part outside the band indicates that it decays faster with distance than the expression we will calculate. For $-3<E<-1$ we will pick up only the singularity corresponding to $-2<\varepsilon<0$, namely $\omega = -1$. For $1<E<3$ we reach only the $\omega = +1$ singularity. For $-1<E<1$ we contact both. In all cases we see that the answer will behave like m^{-2} times some phase factor.

We first consider $\varepsilon > 0$.

$$h(k) = k_+ = \cos^{-1}(1-\varepsilon) = \cos^{-1}(1-E-\cos k), \tag{A.15}$$

where we will suppress the unimportant subscript y. Then for application here. Suppose

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$$f(m) \sim \left[\frac{2\pi}{m|h''(k_o)|}\right]^{1/2} g(k_o) \exp\left[-imh(k_o) \mp \frac{i\pi}{4}\,\mathrm{sgn}\,(h''(k_o))\right] \tag{A.14}$$

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We first consider $\mathcal{E} > 0$.

$$h(k) = k_+ = \cos^{-1}(1-\mathcal{E}) = \cos^{-1}(1- E - \cos k), \tag{A.15}$$

where we will suppress the unimportant subscript y. Then

$$h'(k) = -(1-(1-E-\cos k)^2)^{-1/2} \sin k$$

$$h''(k) = -(1-(1-E-\cos k)^2)^{-3/2} (1-E-\cos k) \sin^2 k$$
$$- (1-(1-E-\cos k)^2)^{-1/2} \cos k \quad \text{(A.16)}$$

But $h'(k) = 0$ implies $\sin k_o = 0$. This is satisfied at $k_o = 0, \pm\pi$. Since we don't want to deal with endpoints, and since the integrand is fully periodic, with period 2π, we can shift our domain from $(-\pi,\pi)$ to $(-\pi/2, 3\pi/2)$, for instance. We will have two flat points, at $k = 0$ and $+\pi$.

We find now

$$h(0) = \cos^{-1}(-E)$$

$$h''(0) = -(1-E^2)^{-1/2}$$

$$h(\pi) = \cos^{-1}(2-E)$$

$$h''(\pi) = (1-(2-E)^2)^{-1/2}$$

(A.17)

Since the function must be real on the interval, $k = \pi$ must be the root for $1 < E < 3$, and $k = 0$ for $-1 < E < 1$. For $1 < E < 3$, we thus find

$$G^A_{m+1,1}(E) = \frac{2(\sqrt{2\pi})^2}{(2\pi)^2 m^2} e^{-i\pi/4} (1-(1-E)^2)^{1/4}$$
$$\times (1-(2-E)^2)^{1/4} e^{-im\cos^{-1}(2-E)} e^{-i\pi/4}$$
$$= \frac{2}{2\pi m^2} (1-(2-E)^2)^{1/2} e^{-im\cos^{-1}(2-E)} e^{-i\pi/2}$$
$$= -\frac{2i}{2\pi m^2} \sqrt{(3-E)(E-1)} \left[(2-E) - i\sqrt{(3-E)(E-1)}\right]^m$$

(A.18)

For -1 < E < 1, the k = 0 root contributes:

$$G^{A\,+}_{m+1,1}(E) = \frac{2}{2\pi m^2} e^{-i\pi/4} (1-E^2)^{1/4} (1-E^2)^{1/4} e^{-im\cos^{-1}(-E)} e^{i\pi/4} \tag{A.19}$$

The equations for $\mathcal{E} < 0$ are quite similar. We have

$$h(k) = k_- = \cos^{-1}(-1-\mathcal{E}) = \cos^{-1}(-1-E-\cos k)$$

$$h'(k) = -(1-(-1-E-\cos k)^2)^{-1/2} \sin k$$

$$h''(k) = -(1-(-1-E-\cos k)^2)^{-1/2}(-1-E-\cos k)\sin^2 k$$
$$-(1-(-1-E-\cos k)^2)^{-1/2}\cos k \tag{A.20}$$

Again, the flat points are at k = 0, π.

$$h(0) = \cos^{-1}(-2-E)$$
$$h''(0) = -(1-(-2-E)^2)^{-1/2}$$
$$h(\pi) = \cos^{-1}(-E) \tag{A.21}$$
$$h''(\pi) = (1-E^2)^{-1/2}$$

For -3 < E < -1, the real root is k = 0, so

$$G^{A}_{m+1,1}(E) = \frac{-2(\sqrt{2\pi})^2}{(2\pi)^2 \; m^2} e^{i\pi/4} (1-(1+\mathcal{E})^2)^{1/4}\Big|_{\mathcal{E}=E+1}$$
$$\times (1-(-2-E)^2)^{1/4} e^{i\pi/4} e^{-im\cos^{-1}(-2-E)}$$
$$= -\frac{2}{2\pi m^2}\sqrt{(-1-E)(E+3)}\, e^{-im\cos^{-1}(-2-E)} e^{i\pi/2}$$
$$= -\frac{2i}{2\pi m^2}\sqrt{(-1-E)(E+3)}\left[(-2-E)-i\sqrt{(-1-E)(E+3)}\right]^m \tag{A.22}$$

Finally, for -1 < E < 1, we add the k = π root to G^+_{ij} of eqn. (A.19) to obtain

$$G^{A}_{m+1,1}(E) = G^{+}_{ij} + \left(-\frac{2}{2\pi m^2}\right) e^{i\pi/4} (1-E^2)^{1/4} (1-E^2)^{1/4}$$
$$\times e^{-im\cos^{-1}(-E)} e^{-i\pi/4}$$
$$= G^{+}_{ij} - G^{+}_{ij} = 0 \quad \text{to order } \frac{1}{m^2}$$

We can summarize G

$$G^{A}_{m+1,1}(E) = \begin{cases} -\frac{i}{\pi m^2}\sqrt{(3-|E|)(|E|-1)}\left[(2-|E|)\,\mathrm{sgn}(E) - i\sqrt{(3-|E|)(|E|-1)}\right]^m, & 1<|E|<3 \\ 0 & \text{otherwise} \end{cases} \qquad \text{(A.23)}$$

We should check whether $G^{A}_{m+1,1}$ (E) satisfies the symmetry remarks catalogued in Section III.B. Since (2-|E|) sgn E is odd in E, while $\sqrt{(3 - |E|)(|E| - 1)}$ is even, we find (remark 3) that ImG and ReG do have the opposite symmetry with respect to inversion of the band (E →-E). Also, for example, $\mathrm{Im}G^{A}_{m+1,1}$ and $\mathrm{Im}G^{A}_{m+2,1}$ have opposite energy inversion symmetries. From the form of the phase factor we see that the number of nodes and extrema increases linearly with m (remark 6); it is not clear how they increase in the center of the band, where higher order terms determine behavior. Obviously $\mathrm{Im}G_{ij}$ vanishes outside the band (remark 5), since G_{ij} does. However, the asymptotic ImG grows initially with the 1/2 rather than 3/2 poiwer of $|E - E_o|$, the energy above the bottom of the band (or below the top), and is initially negative at the bottom of the band.

This apparent discrepancy warrants closer scrutiny. We let $\epsilon = |E - E_o|$ be the energy away from the band edge, toward the band interior. For $\epsilon \ll W_b$, we can write $\mathrm{Im}G_{11}(E,k_\parallel) = \epsilon - k_\parallel^2$. It then follows that

$$\mathrm{Im}\, G^A_{m+1,1}(-E_0+\epsilon) = 2\pi \int_0^{\sqrt{\epsilon}} J_0(km)\, k\sqrt{\epsilon - k^2}\, dk$$
$$= 2\pi\, \epsilon^{3/2} \int_0^1 J_0(st)\, t\sqrt{1-t^2}\, dt, \tag{A.24}$$

where we have set $t \equiv k/\sqrt{\epsilon}$ and $s \equiv m\sqrt{\epsilon}$, and J_o is the Bessel function of zero order. For $\epsilon < m^{-2}$, i.e. $s \leq 1$, the Bessel function can be replaced by unity, and we find the advertised behavior, $\mathrm{Im}G \propto +\epsilon^{3/2}$. For $s \gg 1$, we can check our asymptotic expression. Using the asymptotic expression for J_o, we have

$$\mathrm{Im}\, G^A_{m+1,1}(-E_0+\epsilon) \sim 2\pi\, \epsilon^{3/2} \sqrt{\frac{2}{\pi s}}\, \mathrm{Re}\, e^{-i\pi/4} \int_0^1 e^{ist}\, t\sqrt{1-t^2}\, dt \tag{A.25}$$

Recalling eqn. (A.9), we see that

$$\int_0^1 e^{ist}\, t\sqrt{1-t^2}\, dt \simeq \sqrt{2}\, I_-(1) = \sqrt{\frac{\pi}{2}}\, e^{-3\pi i/4}\, e^{is}\, s^{-3/2}$$

Hence

$$\mathrm{Im}\, G^A_{m+1,1}(-E_0+\epsilon) \sim -2\pi\, \epsilon^{3/2}\, s^{-2}\, \mathrm{Re}\, e^{is}$$
$$= -\frac{2\pi}{m^2}\, \epsilon^{1/2} \cos m\sqrt{\epsilon} \tag{A.26}$$

reproducing the $(\epsilon^{1/2}/m^2) \times$ phase factor behavior of eqn. (A.23

The most surprising aspect of the asymptotic form of $G_{i+m,1}$ is its vanishing in the center of the band. Certainly, as Fig. 4.1 suggests, this is not the case for nearest neighbor Green's functions. To ascertain the limits of the reliability of our asymptotic expression, we have compared directly the Green's functions calculated by Kalkstein and Soven's program with those predicted by the asymptotic form. Table A-1 displays the results for m = 1, 3, and 7. We find that for m ≥ 3, the asymptotic form does give a fair accounting of the exact behavior. For m ≥ 7, the decrease in the size of G(E) in the center third of the band is as precipitous as our equation (A.23) suggests. For m = 1 and m = 2, (nearest and third nearest neighbors), the asymptotic formula is completely invalid, as our comments on the exponential-like fall-off of the interaction energy for small separations requires. This is in sharp distinction to Caroli's(C2) findings for the asymptotic form of the (Anderson-model indirect) interaction between localized bulk magnetic impurities. He finds that even for nearest neighbors, the asymptotic formula gives the same energy, to within a factor of two, of a more exact expression. However, this more exact expression embodies some approximations untenable for us (in particular, that $V^2G^X(E)$ can be replaced by a constant),

Table A.1. Exact and asymptotic Green's functions in the <10> direction.

$m=1$

E	$\mathrm{Im}\,\hat{G}_{m+1,1}(E)^{asym}$	$\mathrm{Im}\,\hat{G}_{m+1,1}(E)$	$\mathrm{Re}\,\hat{G}_{m+1,1}(E)^{asym}$	$\mathrm{Re}\,\hat{G}_{m+1,1}(E)$	$\lvert\hat{G}_{m+1,1}(E)^{asym}\rvert$	$\lvert\hat{G}_{m+1,1}(E)\rvert$
-3.0	0.0	0.0000	0.0	-0.1003	0.0	0.1003
-2.8	-0.1528	0.0254	-0.1146	-0.1363	0.1910	0.1386
-2.6	-0.1528	0.0682	-0.2037	-0.1565	0.2546	0.1707
-2.4	-0.1167	0.1177	-0.2674	-0.1614	0.2917	0.1998
-2.2	-0.0624	0.1694	-0.3056	-0.1509	0.3119	0.2269
-2.0	0.0000	0.2199	-0.3183	-0.1258	0.3183	0.2533
-1.8	0.0624	0.2656	-0.3056	-0.0864	0.3119	0.2793
-1.6	0.1167	0.3037	-0.2674	-0.0338	0.2917	0.3056
-1.4	0.1528	0.3304	-0.2037	0.0319	0.2546	0.3320
-1.2	0.1528	0.3411	-0.1146	0.1101	0.1910	0.3584
-1.0	0.0	0.3253	0.0	0.2002	0.0	0.3820
-0.8	0.0	0.2737	0.0	0.2725	0.0	0.3862
-0.6	0.0	0.2129	0.0	0.3248	0.0	0.3883
-0.4	0.0	0.1454	0.0	0.3617	0.0	0.3899
-0.2	0.0	0.0736	0.0	0.3838	0.0	0.3908
0.0	0.0	0.0	0.0	0.3911	0.0	0.3911

$m=3$

E	$\mathrm{Im}\,\hat{G}_{m+1,1}(E)^{asym}$	$\mathrm{Im}\,\hat{G}_{m+1,1}(E)$	$\mathrm{Re}\,\hat{G}_{m+1,1}(E)^{asym}$	$\mathrm{Re}\,\hat{G}_{m+1,1}(E)$	$\lvert\hat{G}_{m+1,1}(E)^{asym}\rvert$	$\lvert\hat{G}_{m+1,1}(E)\rvert$
-3.0	0.0	0.0000	0.0	-0.0109	0.0	0.0109
-2.8	0.0075	0.0179	-0.0199	-0.0152	0.0212	0.0235
-2.6	0.0265	0.0307	-0.0100	0.0006	0.0283	0.0307
-2.4	0.0306	0.0288	0.0107	0.0214	0.0324	0.0359
-2.2	0.0197	0.0144	0.0285	0.0367	0.0347	0.0394
-2.0	-0.0000	-0.0065	0.0354	0.0416	0.0354	0.0421
-1.8	-0.0197	-0.0269	0.0285	0.0337	0.0347	0.0431
-1.6	-0.0306	-0.0392	0.0107	0.0151	0.0324	0.0424
-1.4	-0.0265	-0.0377	-0.0100	-0.0055	0.0283	0.0381
-1.2	-0.0075	-0.0235	-0.0199	-0.0199	0.0212	0.0308
-1.0	0.0	-0.0065	0.0	-0.0136	0.0	0.0151
-0.8	0.0	-0.0103	0.0	-0.0079	0.0	0.0130
-0.6	0.0	-0.0129	0.0	-0.0109	0.0	0.0163
-0.4	0.0	-0.0122	0.0	-0.0155	0.0	0.0198
-0.2	0.0	-0.0074	0.0	-0.0204	0.0	0.0217
0.0	0.0	0.0000	0.0	-0.0227	0.0	0.0227

$m=7$

E	$\mathrm{Im}\,\hat{G}_{m+1,1}(E)^{asym}$	$\mathrm{Im}\,\hat{G}_{m+1,1}(E)$	$\mathrm{Re}\,\hat{G}_{m+1,1}(E)^{asym}$	$\mathrm{Re}\,\hat{G}_{m+1,1}(E)$	$\lvert\hat{G}_{m+1,1}(E)^{asym}\rvert$	$\lvert\hat{G}_{m+1,1}(E)\rvert$
-3.0	0.0	0.0000	0.0	-0.0009	0.0	0.0009
-2.8	0.0008	-0.0001	0.0038	0.0040	0.0039	0.0040
-2.6	-0.0051	-0.0051	-0.0011	-0.0018	0.0052	0.0054
-2.4	0.0015	0.0021	-0.0058	-0.0059	0.0060	0.0063
-2.2	0.0063	0.0066	0.0010	0.0017	0.0064	0.0068
-2.0	-0.0000	-0.0005	0.0065	0.0066	0.0065	0.0066
-1.8	-0.0063	-0.0068	0.0010	0.0013	0.0064	0.0070
-1.6	-0.0015	-0.0020	-0.0058	-0.0055	0.0060	0.0059
-1.4	0.0051	0.0047	-0.0011	-0.0014	0.0052	0.0049
-1.2	-0.0008	-0.0002	0.0038	0.0042	0.0039	0.0042
-1.0	0.0	-0.0001	0.0	-0.0010	0.0	0.0010
-0.8	0.0	0.0000	0.0	-0.0004	0.0	0.0004
-0.6	0.0	0.0004	0.0	0.0009	0.0	0.0010
-0.4	0.0	-0.0010	0.0	0.0011	0.0	0.0015
-0.2	0.0	-0.0011	0.0	-0.0001	0.0	0.0011
0.0	0.0	0.0000	0.0	-0.0006	0.0	0.0006

and relies on a free electron picture to obtain that asymptotically

$$G_{1,R}(E) \sim \frac{e^{i\sqrt{E}\,R}}{\sqrt{E}\;R}\; G_{11}(E)$$

We are now ready to find the asymptotic form of the pair interaction to lowest order in $(\frac{1}{m})$. For $E_F \leq -1$, we find that equation (A.1) becomes

$$\Delta W^{A}_{m+1,1} \sim \frac{2}{\pi}\,\mathrm{Im}\, V^4\left(-\frac{1}{\pi^2 m^4}\right) \times \int_{-3}^{E_F} \bar{G}^{A\,2}_{aa}\,(3+E)(-1-E)\, e^{-2im\cos^{-1}(-2-E)}\, dE \qquad \text{(A.27)}$$

We make the charge of variable $t \equiv \cos^{-1}(-2-E)$, and accordingly define $t_F \equiv \cos^{-1}(-2-E_F)$. Then

$$\Delta W^{A}_{m+1,1} \sim \frac{2}{\pi}\,\mathrm{Im}\, V^4\left(-\frac{1}{\pi^2 m^4}\right)\int_0^{t_F} \bar{G}^{A\,2}_{aa}(E(t))\,\sin^2 t\; e^{-2imt}\, dt.$$

(A.28)

Since the integrand is smooth in t, there are no internal critical points. We can therefore find the asymptotic form using the integration by parts technique. (See Ref. E3):

$$\Delta W^{A}_{m+1,1} \sim \frac{2}{\pi}\,\mathrm{Im}\, V^4\left(-\frac{1}{\pi^2 m^4}\right) \times \left\{ \bar{G}^{A\,2}_{aa}(E(t))\,\sin^2(t)\,\frac{e^{-2imt}}{-2im}\Big]_0^{t_F} + O\left(\frac{1}{m^2}\right)\right\} \qquad \text{(A.29)}$$

For $E_F = -1$, $t_F = \pi$, and the integrated term vanishes. We can similarly find the pair interaction in the upper third of the band by integrating down from the top, using the substitute $t = \cos^{-1}(2-E)$. Our result is

$$\Delta W^{A}_{m+1,1}(E_F) \sim \frac{V^4}{\pi m} \operatorname{Re}\left\{ \bar{G}^{A\,2}_{aa}(E_F)\, G^{A\,2}_{m+1,1}(E_F) \right\}$$

so

$$\Delta W^{A}_{m+1,1}(E_F) \sim \int -\frac{V^4}{\pi^2 m^5}(3-|E_F|)(|E_F|-1)\operatorname{Re}\left\{ \left[(2-|E_F|) \times \operatorname{sgn}(E_F) - i\sqrt{(3-|E_F|)(|E_F|-1)} \right]^m \bar{G}^{A\,2}_{aa}(E_F) \right\}, \quad 1 \leq |E_F| < 3$$

$$\Delta W^{A}_{m+1,1}(E_F) \sim 0 \qquad \text{otherwise}$$

We have thus found that the pair interaction falls off as the fifth power of distance in the <10> direction, for the band less than a third filled or more than 2/3 filled. In the middle third, the interaction decays even faster. This fact no doubt contributes to our finding exponential-like decay in the interaction. However, its appearance for $X \neq A$ suggests that in fact inverse power behavior does not hold within a few lattice spacings.

It is natural to ask what happens in other directions. The energy factors will be different. The actual computations are quite messy. If we try an integration in the k_x and k_y directions, as above, we find that the resulting G goes as $m^{-3/2}n^{-1/2}$ or $n^{-3/2}m^{-1/2}$, depending on which direction we do first. This suggests that we rotate perpendicular axes, so that one points along the direction adjoining the two adatoms. However, the endpoints are then quite complicated. (Presumably if we write $n = \alpha m$, and grind through the morass, our answer should be invariant to $\alpha \to 1/\alpha$.)

The sole exception to this statement is the <11> direction. The rotation of axes can be characterized by the change of variables

$$k_+ = (k_x + k_y)/2 \quad , \qquad k_- = (k_x - k_y)/2$$

Then equations (A-2), (A-3), and (A-13), combined, are transformed to

$$G^{A}_{m+1,\, m+1}(E) = \frac{4}{(2\pi)^2}\int_0^{\pi} dk_- \int_{-(\pi-k_-)}^{\pi-k_-} dk_+ \; e^{2imk_+} \; 2\left(\omega + i\sqrt{1-\omega^2}\right),$$

$$\omega = E + 2\cos k_+ \cos k_-$$

This double integral can then be attacked in a manner similar to the <10> problem. The k_+ integration is performed using Lighthill's generalized function technique (eqn.s A.7, A.8, and A.9). Subsequently we do a stationary phase integration over k_-. We find the same result as when we use an alternative approach, namely, first doing the k_x integration, which is identical to eqn. (A.3), and consequently gives us eqns. (A.10) and (A.12). The stationary phase integral is changed however; we now find

$$h(k) = \cos^{-1}(\pm 1 - E - \cos k) - k$$

We again find flat points, this time where $\cos k_o = \frac{\pm 1 - E}{2}$.

This equation suggests that there are a total of eight flat points, but other considerations (the value of $\sin k_o$) show there are only four: two for each sign of 1, with one between $-\pi/2$ and 0 and the second between $\pi/2$ and π, in each case. In all cases we find that

$$|h''(k_0)| = |\cot k_0|$$

Determining the phase factor is somewhat tricky; the easiest method is to just pick the value giving agreement with the computed values. We find that

$$G^{A}_{m+1,\,m+1}(E) \sim \begin{cases} -\dfrac{i}{2\pi m}\sqrt{\dfrac{(3-|E|)(|E|+1)}{(|E|-1)}}\left[\dfrac{1-|E|}{2}\,\mathrm{sgn}\,E - i\sqrt{(3-|E|)(|E|-1)}\right]^{2m}, & 1<|E|<3 \\ \dfrac{1}{2\pi m^2}\left\{-\sqrt{\dfrac{(3+E)(1-E)}{1+E}}\left[\dfrac{-1-E}{2}-\dfrac{i}{2}\sqrt{(3+E)(1-E)}\right]^{2m} + \sqrt{\dfrac{(3-E)(1+E)}{1-E}}\left[\dfrac{1-E}{2}-\dfrac{i}{2}\sqrt{(3-E)(1+E)}\right]^{2m}\right\}, & -1<E<1 \end{cases}$$

We observe that $\mathrm{Im}G_{m+1,m+1}$ is even, while its real part is odd in E, (i.e. $G(-E) = -G^*(E)$), as required (remark 3). Again we find m^{-2} decay with a phase factor raised to the m^{th} power. However, now the Green's function is non-vanishing in the interior third of the band, and the singularities at ± 1 are $|\,|E| - 1|^{-1/2}$ rather than $|\,|E| - 1|^{1/2}$ as in the <10> direction. We still find +1/2 singularities at the band edges. The singularities at $E = \pm 1$ indicate that G falls off more slowly at these energies. Indeed, a closer inspection shows that at these two values, h(k) can become a constant. The asymptotic expression does not fit the actual Green's function very well until m = 4, farther than in the <10> case. That it works reasonably well in that case is verified by the display of computation in Table A-2.

The calculation of the pair interaction energy proceeds as before. We set $t = \cos^{-1}\left(\frac{\pm 1 - E}{2}\right)$ and integrate by parts to find

$$\Delta W^{A}_{m+1,\,m+1} \sim \frac{V^4}{\pi m} \mathrm{Re}\left\{ \bar{G}^{A\,2}_{aa}(E_F)\, G^{A\ \ 2}_{m+1,\,m+1}(E_F) \right\}$$

$$\sim m^{-5}$$

We fully expect, but cannot explicitly verify, that this R^{-5} decay holds for arbitrary direction. The detailed behavior is highly dependent on direction and Fermi energy. The pair interaction is oscillatory in E_F and R and anisotropic.

Table A.2

Tabulation for comparison of exact Green's functions with their asymptotic values, in the <11> direction.

E	$Im\, G_{55}^{A}(E)^{asym}$	$Im\, G_{55}^{A}(E)$	$Re\, G_{55}^{A}(E)^{asym}$	$Re\, G_{55}^{A}(E)$	$\lvert G_{55}^{A}(E)\rvert^{asym}$	$\lvert G_{55}^{A}(E)\rvert$
-3.0	0.0	0.0000	0.0	-0.0017	0.0	0.0017
-2.8	0.0058	0.0045	0.0029	0.0047	0.0065	0.0065
-2.6	-0.0040	-0.0060	0.0086	0.0069	0.0094	0.0091
-2.4	-0.0120	-0.0107	-0.0010	-0.0044	0.0120	0.0115
-2.2	-0.0061	-0.0020	-0.0132	-0.0140	0.0145	0.0141
-2.0	0.0086	0.0119	-0.0149	-0.0110	0.0172	0.0162
-1.8	0.0202	0.0183	-0.0031	0.0036	0.0204	0.0186
-1.6	0.0187	0.0103	0.0159	0.0192	0.0245	0.0218
-1.4	0.0012	-0.0096	0.0308	0.0235	0.0308	0.0254
-1.2	-0.0308	-0.0299	0.0318	0.0077	0.0443	0.0309
-1.0	0.0	-0.0288	0.0	-0.0309	0.0	0.0422
-0.8	0.0347	0.0169	-0.0366	-0.0338	0.0504	0.0378
-0.6	0.0394	0.0332	0.0052	-0.0003	0.0397	0.0332
-0.4	0.0149	0.0147	0.0306	0.0252	0.0341	0.0292
-0.2	-0.0162	-0.0135	0.0263	0.0233	0.0309	0.0269
0.0	-0.0298	-0.0262	0.0	0.0	0.0298	0.0262